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Research in Nitropolymers and Their Application to Solid Smokeless

Propellants. 15 June 1954. L. T. Carleton, J. K. Elder, J. R. Fischer, R. D. Hamlin, R. L. Parrette, C. R. Vazmonian. 50 pp., 13 tables, 4 figs., 2 appendixes. Aerojet-General Corp. Rept. No. 833 (Quarterly) (Contract N7 onr-462, Task Order 1). CONFIDENTIAL. See also: 14, 181.

The emulsion polymerization of 2,2-dinitrobutyl acrylate was advanced from runs made in small vials to runs in larger containers. Stable emulsions were obtained, but the conversion did not exceed 70% at 45°C. in six to seven hours. The addition of small amounts of ferrous ion increased the rate of polymerization, while larger amounts had an adverse effect.

As the normal rate of polyurethane formation is so very slow, a practical method must make use of some means of catalysis. A series of newly prepared chelated-metal compounds were tested and compared with iron(III) acetylacetonate. This catalyst is still by far the most active catalyst for the polymerization reaction. Other metal acetylacetonates did not show a pronounced catalytic activity for the polyurethane formation, but several are suitable catalysts for the homopolymerization of the diisocyanate.

The following two new polyurethanes were prepared from 2-nitroazabicyclo-1,4-butane diisocyanate: XV-N from ethylene glycol and XV-O from 5,5-dinitro-1,2-hexanediol. Polyurea XV-C was prepared from the same diisocyanate and water. All these polymers were characterized by elemental analysis, relative viscosity, softening points, and stability tests.

A new polyurethane, I-P, was prepared from 3,3-dinitro-1,5-pentane diisocyanate and 3-nitroazabicyclo-1,5-pentanediol. Postnitration yielded Polyurethane I-PN, a polymer with an estimated specific impulse of 207 lbf-sec/lbm. The new polymers were characterized by elemental analysis, heats of combustion, softening point, and relative viscosity.

In order to control the degree of branching and crosslinking of linear polymers, a part of the diol was replaced by ethanediolamine in the polymer system. The resulting urea linkages became crosslinked with

an excess of the diisocyanate. It was found that this crosslinking was effected in 50% dioxan solution. The polymers were characterized by elemental analysis, heats of combustion, softening point, and relative viscosity. The polymers were characterized by elemental analysis, heats of combustion, softening point, and relative viscosity.

Phthalate Substitutes for DNT. Deterrent Coatings for Single-Base Propellants. July 1954. H. A. Aaronson, F. R. Schwartz, E. Budnick. 16 pp., 8 tables. Picatinny Arsenal Tech. Rept. Serial No. 2031 (Ord proj. TAI-5006B, Item g). CONFIDENTIAL.

14, 274

The interaction of diamminoguanidinium iodide and excess tetrazolodiazonium hydroxide, in the presence of one equivalent of sodium acetate, resulted in a 22% yield of tetrazene. The tetrazonium salt derived from sym-diaminotetrazine failed to undergo coupling reactions with hydrazine, sym-dimethylhydrazine, or aminoguanidine. The diazonium salt derived from 3-amino-1,2,4-triazole failed to undergo coupling with hydrazine or sym-diacetylhydrazine but formed a very sensitive solid on interaction with hydrazine. It was found that 1,6-bis-p-chlorophenyl-3,4-dimethyl-1,5-hexadiene is cleaved by the action of cold, concentrated sulfuric acid, resulting in the regeneration of the corresponding coupling agents, namely, the p-chlorobenzene diazonium ion and sym-dimethylhydrazine. The first of these coupling agents was isolated, by treatment of the acid solution with β-naphthol, as a 98% yield of 2-hydroxy-4-chloro-1-naphtheneazobenzene; the other coupling agent was isolated as a 58% yield of N,N'-dimethyl-N,N'-dibenzoylhydrazine.

one reaction, perhaps indicating resinification of appreciable amounts of the diazonium intermediate.

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Report No. 833

RESEARCH IN NITROPOLYMERS AND THEIR
APPLICATION TO SOLID SMOKELESS PROPELLANTS

Contract N7onr-462, Task Order I

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AEROJET-GENERAL CORPORATION

Azusa, California

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CONTRACT FULFILLMENT STATEMENT

This quarterly report is submitted in partial fulfillment of Contract N7onr-462, Task Order I.

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I. SUMMARY

A. This quarterly summary covers research conducted in partial fulfillment of Contract N7onr-462, Task Order I, during the period from 16 February through 15 May 1954.*

B. Work on Contract NOas 53-618-c, previously discussed in these reports, has been completed, and a final report (Aerojet Report No. 817) has been issued. This work is now being continued under Contract NOas 54-329-c and will be reported in the next quarterly period.

C. The most important results on Contract N7onr-462, Task Order I, are summarized below:

start
was
5th The emulsion polymerization of 2,2-dinitrobutyl acrylate ~~has been~~ advanced from runs made in small vials to runs in larger containers. Stable emulsions were obtained, but the conversion did not exceed 70% at 45°C. in 6 to 4 hours. The addition of small amounts of ferrous ion increased the rate of polymerization, while larger amounts had an adverse effect.

para *As* The normal rate of polyurethane formation is so ~~slow~~ *very slow*, ~~that~~ a practical method must make use of some means of catalysis. A series of newly prepared chelated-metal compounds ~~have been~~ tested and compared with iron(III) acetylacetonate. This catalyst is still by far the most active catalyst for the polymerization reaction. Other metal acetylacetonates did not show a pronounced catalytic activity for the polyurethane formation, but several are suitable catalysts for the homopolymerization of the diisocyanate.

para *two* *were* The following ~~new~~ polyurethanes ~~have been~~ prepared from 2-nitroazirane-1,4-butane diisocyanate; ~~in addition to those reported previously.~~

~~polyurea~~

XV-N from

Ethylene glycol and

XV-O from

5,5-Dinitro-1,2-hexanediol. *←*

was
work Polyurea XV-E ~~has been~~ prepared from the same diisocyanate and water. All these polymers ~~have been~~ characterized by elemental analysis, relative viscosity, softening points, and stability tests.

para A new polyurethane, I-P, was prepared from 3,3-dinitro-1,5-pentane diisocyanate and 3-nitroazirane-1,5-pentanediol. Postnitration yielded

* Previous work on Contract N7onr-462, Task Order I, was covered in Aerojet Reports No. 330, 345, 371, 386, 386A, 494, 417, 417A, 424, 457, 461, 466, 482, 495, 515, 540, 563, 590, 622, 638, 663, 686, 700, 720, 740, 772 and 807.

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was replaced

I Summary, C (cont.)

In order to control the degree of branching and crosslinking of linear polymers,

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Polyurethane I-PN, a polymer with an estimated specific impulse of 207 lbf-sec/lbm. The new polymers have been characterized by elemental analysis, heats of combustion, softening point, and relative viscosity.

~~In modifying linear polymers in order to obtain the best physical and mechanical properties, it is necessary to control the degree of branching and crosslinking. This modification was sought by replacing a part of the diol by ethanclamine in the polymer system. The resulting urea linkages would then be crosslinked with an excess of the diisocyanate. It was found that this crosslinking was effected in 50% dioxan solution at 65°C. after a reaction time of 500 hours. Another means for introducing crosslinking was found by heating the linear polymer 24 hours at 80 to 100°C.~~

The use of ethanclamine as a "built-in" modifying element in polyurethanes has the disadvantage that the specific impulse of the polymer is reduced. Previous studies have shown that nitropolyureas can be prepared from nitrodiisocyanates and water. By using water to produce amino groups within the reaction, the amine then reacts with the isocyanates, causing polyurea formation. In this way the loss of specific impulse of the modified nitropolyurethane is minimized.

~~Formulation studies in the past dealt with the exploration of various methods suitable for the manufacture of a nitropolymer propellant. This led to the discovery of various casting procedures as well as the formulation of extruded rods containing inorganic oxidizers.~~

on formulation studies
The work dealt primarily with the formulation of flat sheets, required for evaluation of the rheological properties. Other work dealt again with the incorporation of various amounts of inorganic oxidizers. All these products have been characterized by burning rates, thermal stability, and impact stability. Another problem was the introduction of crosslinking in a second-stage curing, because it was observed that insoluble crosslinked polymers are partly degraded in milling operations. In order to restore the tridimensional structure of the polymer, a post-formulation cure is required. Attempts to effect this crosslinking with formaldehyde or glyoxal were not successful.

~~Plasticization of nitropolymer is an essential part of formulation work. In order not to sacrifice specific impulse plasticizers containing nitro groups are desired. Several nitro plasticizers gave poor, bubbly castings in recent formulation runs, where the same had previously given satisfactory formulations. It has been found that the extremely sensitive nature of the monomers demands highest purity in plasticizer, in order to avoid any side reactions caused by the extreme reactivity of the isocyanate function. Carefully purified plasticizer passed both the Warburg and the KI-starch paper test and gave bubble-free gels.~~

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I Summary, C (cont.)

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para 12
Two commercial plasticizers, dibutyl phthalate and tricresyl phosphate, gave strong, rubbery products with Polyurethane I-A. However, when formulated with inorganic oxidizer, the binder lost strength and the mixture crumbled. ~~It appears that this is due to the presence of nitro-~~
~~groups in the plasticizers.~~

para 13
~~The problems associated with the manufacture of nitro-~~
~~polymers are a direct function of the scale of operation. With the 1-gallon~~
Beken dispersion blade mixer it is possible to obtain data which may be used in the design of larger-scale operations. ~~During the past quarter, a series~~
of polymerizations was conducted in order to gain information with regard to the following: (1) ease of dissipation of heat of reaction, (2) uniformity of product, (3) product reproducibility, (4) method of workup, (5) reaction time, and (6) exclusion of side reactions. ~~Some of these problems are already~~
~~classified, and further work is being conducted to collect additional data.~~

The dissipation of the heat of reaction is readily handled in a homogeneous solution or in a heterogeneous system where a non-solvent such as benzene is used as a heat-transfer medium. Although the latter method gives a dense product, in the single polymerization that was run the reaction was incomplete and gave a low-viscosity product.

Reproducibility and uniformity ^{were} being checked along with stability measurements. Also, several methods of workup involving a minimum of material handling ~~are~~ being studied. The Beken mixer gives fast and thorough mixing, so that the reaction time to produce a polymer does not normally exceed one day.

para 14
The osmometric molecular-weight studies of poly 2,2-dinitro-butyl acrylate ~~have been~~ completed, and the constants in the Staudinger equation have ~~been~~ determined.

para 15
~~Diisocyanate acids and diisocyanates containing nitro-~~
~~groups are the most important intermediates for the preparation of~~
~~polymers. During the past quarter the following new diisocyanates were~~
~~prepared:~~ Two new diisocyanates were prepared, namely-

1. 2,5-Dinitraza-1,6-hexane diisocyanate and
2. 4,11-Dinitraza-1,14-tetradecane diisocyanate.

~~An SPIA data sheet was completed on 2-nitraza-1,4-butane~~
~~diisocyanate and is included as Appendix B.~~

para 16
One of the appendices consists of a completed SPIA data sheet on 2-nitraza-1,4-butane diisocyanate.

End

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II. TECHNICAL PROGRESS: NITROPOLYMERS

A. VINYL POLYMERIZATION

1. Emulsion Polymerization of 2,2-Dinitrobutyl Acrylate

a. Discussion

(1) On the basis of much past experience with the emulsion polymerization of 2,2-dinitrobutyl acrylate in small vials, further experiments were performed on a larger scale, using 6-ounce crown-cap bottles. This method permits sampling of the reaction mixture repeatedly during a run. The basic recipe used contained monomer, water, Atlas Tween 40 emulsifying agent, polyvinyl alcohol stabilizer, and ammonium persulfate catalyst. A number of variations of this recipe were tested in an effort to obtain the best reaction speed, yield, and quality of emulsion.

(2) With one sample of monomer which had been purified by distillation (Specimen A of Table I), the basic recipe plus a small amount of ferrous ion activator gave 70% conversions in 6 to 7 hours of reaction time at 45°C, with smooth, stable emulsions as final products. However, reaction rate and extent of conversion appear to depend greatly on the particular specimen of monomer used; they were much less using the same recipe with specimen B, which had been purified by hexane extraction. It is believed that these best results are associated with high purity of the monomer, and that slight contamination may impair them greatly.

(3) For each of the two specimens of monomer studied, addition of a small amount of ferrous ion activator to the basic recipe increased the rate, at least at first. It also improved the quality of the emulsion. It seems significant that none of the runs in which ferrous ion was added to the basic recipe precipitated out polymer, whereas such precipitation occurred fairly often with the unmodified basic recipe.

(4) Several attempts were made to determine whether "boosting" the reaction with additional activator after the initial fast reaction can increase conversion. Results were inconclusive because of difficulties of sampling and testing.

(5) In general, the rapid test for conversion which was used, based on weighing the total solids precipitated from the sample by methanol, is crude and does not distinguish small differences of behavior. Another difficulty is the fact that at high conversions the mixture becomes so viscous that a sample can no longer be withdrawn into a syringe.

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II Technical Progress, A (cont.)

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(6) However, in spite of the need for better control, some further main conclusions can still be drawn from the results. In Table I, the results are grouped so as to illustrate these points most conveniently.

(a) While use of a small amount of ferrous ion activator (a few milligrams /20 ml monomer) was beneficial, increasing the amount (in the case of monomer B) caused the reaction to level off at low conversions, and an increase to 100 mg/20 ml monomer suppressed the reaction almost completely.

(b) Other schemes of activation were applied to the basic recipe, i.e., complexing the ferrous ion with sodium pyrophosphate, and the addition of diethylene triamine and sodium thiosulfate as activators. However, these produced longer ultimate reaction times or lower ultimate conversions, although the triamine, at least, probably increased the initial rate.

(c) A few experiments were performed in decreasing the amount of catalyst used, and in substituting potassium persulfate for ammonium persulfate. The amount of catalyst appears not to have much influence on rate of conversion; substitution of the potassium salt may increase the rate somewhat. The poor quality of the products obtained is not encouraging.

(7) The conclusion is drawn that enough is now known about formulation to permit an increase of scale of the production of polydinitrobutyl acrylate, and an application of the process to other monomers, particularly 2,2-dinitropropyl acrylate. Since monomer purity is essential in obtaining satisfactory emulsions some work must be directed toward closer control of the quality of the product. In addition, studies of improvement of formulation will be continued as time permits.

b. Experimental

(1) The basic recipe used for emulsion polymerization was the following:

20 ml dinitrobutyl acrylate monomer
0.25 g polyvinyl alcohol in 20 ml water, as
stabilizer
1.70 g Atlas Tween 40, as emulsifier
0.25 g $(\text{NH}_4)_2\text{S}_2\text{O}_8$ in 2 ml water, as catalyst

In the work reported here, this recipe was used without change, or was altered by the inclusion of additives or by substitution of catalyst.

(2) All components of the emulsion polymerization recipe, except catalyst and accelerator, were placed in a 6-oz bottle, which was then thoroughly purged of air by bubbling nitrogen through it for several minutes. A 1-in. disk of 1/16-in.-thick Hycar was then placed on top, protected on the inner side by a thin disk of polythene. A standard crown

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II Technical Progress, A (cont.)

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cap was placed over this, and sealed on with a hand-operated bottle capper. The cap had been specially prepared by removing the inner cork liner, drilling a 2-mm diameter hole in the center, and cementing a disk of polythene over the hole. Thorough directions for the preparation of such closures have been given in the literature*.

(3) Just before the reaction was started, solutions of catalyst and accelerator (if required) were injected into the reaction mixture with a hypodermic syringe. Using the same syringe, a homogeneous sample of the complete charge was withdrawn for a blank determination of the amount insoluble in ethanol. The bottle was then rotated end-over-end in a water bath maintained at 45°C. At timed intervals the bottle was removed, and other samples were withdrawn for determination of the extent of reaction.

(4) This determination was made on a 2-gram sample by discharging it into 20 ml of ethanol, decanting the liquid layer, and washing, drying and weighing the precipitate. The weight of dried solid, corrected for the insolubles in the blank determination, represents the amount of polymer formed.

(5) Results of this test for all runs are given in Table I. Several values of the amount reacted are believed to be in error because of faulty technique. The erroneous values appear to be high more often than low, indicating that there may have been some separation of the emulsions at low conversions.

(6) After completion of each run, the quality of the emulsion was noted (Table I). Some few of the products were worked up to determine final conversions. Contents of the bottle were transferred to 100 ml of methanol, which cleanly precipitated the solids. These solids were then thoroughly washed with acetone to dissolve the polymer from the adherent polyvinyl alcohol. The washings were filtered and concentrated, then poured into 20 volumes of hexane to re-precipitate polymer, and the polymer was vacuum dried. The results for the few specimens worked up in this way are given in Table I. Molecular weights were determined by measuring relative viscosities, and converting these by the method of Section V.

(7) Two specimens of monomer were used. Specimen A was obtained from a composite of early preparations by first treating with hexane to eliminate polymer, and distilling the hexane-soluble material from methylene blue at reduced pressure; $n_D^{25} = 1.4582$. Specimen B was purified only by washing free from polymer with hot hexane in the presence of activated alumina; $n_D^{25} = 1.4601^{**}$.

* C. F. Fryling, Ind. Eng. Chem. 40, 928-932 (1946); S. A. Harrison and E. R. Meinelke, Anal. Chem. 20, 47-48 (1948).

** Report No. 807, p. 9.

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TABLE I

EMULSION POLYMERIZATION OF 2,2-DINITROBUTYL ACRYLATE IN BOTTLES AT 45°C

With Monomer Specimen A

	Run	Time hr	% Reacted		Appearance of Final Emulsion	Polymer M. W.
			From Test	From Work-up		
<u>Basic Recipe</u>	4/22/A	3 1/2	39		Slightly uneven	180,000
		6 1/2	65			
		7	—	54		
	4/22/B	3 1/2	45		Smooth; slight separation of water layer in several days	
		6 1/2	53			
		23	Clogs*			
<u>Basic Recipe + 3 mg FeSO₄·7H₂O/1 ml H₂O</u>	4/22/C	3 1/2	48		Smooth	150,000
		6 1/2	68			
		7	—	73		
	4/22/D	3 1/2	46		Smooth; slight separation of water layer in several days	
		6 1/2	66			
		23	Clogs			
Boosted with same activator— at 6 hr	4/15/A	3	49		Smooth; separation of water layer in several days	
		6	59			
		23 1/2	Clogs			
	4/15/B	3	57			
		6	72			
		23 1/2	Clogs	69		
Boosted with same activator— at 6 hr	4/7/C	17	Clogs		—	130,000
		40 1/2	—	70		
	4/15/C	2 1/2	35		Smooth; separation of water layer in several days	
		5 1/2	31			
		23	Clogs			
(Complex Solution is 2.0 g FeSO ₄ ·7H ₂ O + 3.0 g Na ₄ P ₂ O ₇ ·10H ₂ O + 20 ml water)	4/15/D	2 1/2	32		—	
		5 1/2	47			
		23	34			

*Clogs needle when sampling is attempted.

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TABLE I (cont.)

With Monomer Specimen B

	Run	Time, hr	% Reacted		Appearance of Final Emulsion	Polymer M. W.
			From Test	From Work-up		
<u>Basic Recipe</u>	2/18/A	2 1/4	3		Fairly smooth; marked separation of water in several days	
		4	7			
		21	56			
		27	48			
	2/23/A	2 1/4	7		Smooth, quick separation of water	
		4 1/2	24			
		6 1/2	13			
	3/23/1	16	38		—	
		19 1/2	45			
	3/25/A	2	10		Immediate polymer* separation	
		4	25			
		6	19			
		24 1/2	polymer out			
<u>Basic Recipe + FeSO₄ · 7H₂O solutions 3 mg/1 ml H₂O</u>	3/25/F	2	9		Smooth; separation of water layer in several days	
		4	18			
		6	27			
	3/24/G	16 1/2	32		Same	
		23	54			
	4/1/A	1 1/2	7			
		4	19			
		5 1/2	36			
		7	25			
		24	55			
	4/2/A	30	44		Slightly uneven	
		1 1/2	7			
		4	26			
		5 1/2	31			
		7	31			
		24	47			
		30	49			
3 mg/1 ml H ₂ O boosted with 3 mg/1 ml H ₂ O at 19 hr	4/1/E	17	48		Smooth; sepa- ration of water layer in several days	50,000
		19	41			
		21 1/2	43			
		23 1/2	57	49		

* Other experiments, not included, indicate that coagulation of polymer occurs frequently with the basic recipe at about 50% conversion.

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TABLE I (cont.)

With Monomer Specimen B (cont.)

	Run	Time, hr	% Reacted		Appearance of Final Emulsion	Poly M.
			From Test	From Work-up		
10 mg/1 ml H ₂ O	3/25/B	2 4 6 24 1/2	14 26 25 45		Same	
5 mg/1 ml H ₂ O + 2 boosts of 5 ² mg/1/2 ml H ₂ O at 2 and 4 hr	3/26/A	6	27		Same	
25 mg/1 ml H ₂ O boosted with 25 mg/1 ml H ₂ O at 4 hr	2/18/C	2 1/4 4 5 21 27	5 11 11 21 23		Smooth; slight separation of water in several days	
25 mg/ml H ₂ O boosted with 0.25 g (NH ₄) ₂ S ₂ O ₈ / 2 ml H ₂ O at 4 hr	2/18/B	2 1/4 4 5 21 27	5 11 11 21 23		Same	
100 mg/1 ml H ₂ O	2/23/C	2 4 1/2 20 1/2 26	5 4 5 —		Smooth; marked separation of water in several days	
<u>Basic Recipe +</u>						
<u>Other Activators</u>						
0.05 ml diethylene triamine	3/25/C	2 4 6 24 1/2	10 13 16 45		Slightly uneven; separation of water layer in several days	
	3/23/3	16 19 1/2	30 29		—	

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TABLE I (cont.)

With Monomer Specimen B (cont.)

	Run	Time, hr	% Reacted		Appearance of Final Emulsion	Polymer M. W.
			From Test	From Work-up		
0.10 ml diethylene triamine	2/23/D	2	16		Fairly smooth; marked separation of water in several days	
		4 1/2	18			
		20 1/2	36			
		26	45			
0.050 g $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ / 1 ml H_2O	3/25/D	2	8		Smooth; separation of water layer in several days	
		4	6			
		6	9			
		24 1/2	43			
	3/23/L	16	30		—	
		19 1/2	36			

Basic Recipe Except
Catalyst Changed

0.050 g $(\text{NH}_4)_2\text{S}_2\text{O}_8$ / 0.4 ml H_2O	2/23/B	2 1/4	4		Not smooth; quick separation of water	
		4 1/2	29			
		6 1/2	14			
0.050 g $\text{K}_2\text{S}_2\text{O}_8$ / 1 ml H_2O	3/25/E	2	10		Smooth; separation of water layer after several days	
		4	15			
		6	18			
	3/24/F	16 1/2	44		Immediate polymer separation	
		23	polymer out			
0.050 g $(\text{NH}_4)_2\text{S}_2\text{O}_8$ / 1 ml H_2O + 3 mg $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ /1 ml H_2O	4/1/C	1 1/2	7		Same	
		4	18			
		5 1/2	35			
		7	24			
		24	63			
		30	52			
	4/1/D	1 1/2	5		Same	
		4	15			
		5 1/2	13			
		7	18			
		24	65			
		30	48			

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B. ADDITION AND CONDENSATION POLYMERS

1. Polyurethanes

a. Chelated-Metal Compounds as Catalysts for Polyurethane Formation

(1) Introduction

The rate of polyurethane formation, using nitro diols and nitro diisocyanates, is so slow that a practical method for increasing the rate of polymerization was sought. In searching for polyurethane catalysts, the acetylacetonates of vanadium and chromium were studied briefly* before it was found that ferric acetylacetonate was far superior.** This study has now been extended to include other metal acetylacetonates.

(2) Discussion

(a) The rate of polyurethane formation has been studied extensively using the I-J system, 3,3-dinitro-1,5-pentane diisocyanate and 2-nitro-2-methyl-1,3-propanediol, in absolute dioxan, as a model.*** The I-J system was therefore chosen for the comparison of the catalytic activity of other metal acetylacetonates. The experimental results are summarized in Tables II, III, IV, V and Figures 1 and 2.

(b) The rate constants listed in Table II are approximations, inasmuch as some of the more active catalysts also promote the homopolymerization of the diisocyanate. Table III shows the magnitude of this homopolymerization at a larger catalyst concentration used to magnify the effect. Table IV and Figures 1 and 2 show the effect of varying catalyst concentration. This study was made at 35°C in order to lower the rates at high catalyst concentrations into the measurable range.

*Aerojet Report No. 663, p. 13; No. 686, p. 8.

**Aerojet Report No. 686, p. 8

***Aerojet Report No. 590, p. 22; No. 622, p. 18; No. 638, p. 24; No. 663, p. 12; No. 686, p. 8; No. 712, p. 6.

Variation in Rate of Polyurethanes I-J Formation with Catalyst Concentration at 35°C
Initial Concentration in Absolute Dioxan: 1 eq./liter (-OH) and (-NCO)

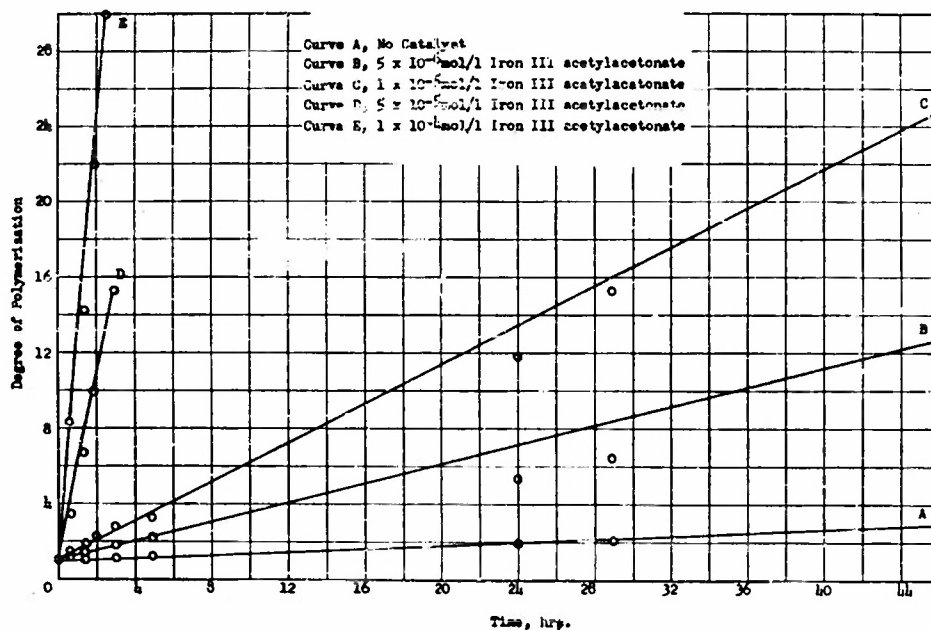


Figure 1

Polyurethanes I-J Rate Constants at 35°C vs. Catalyst Concentration

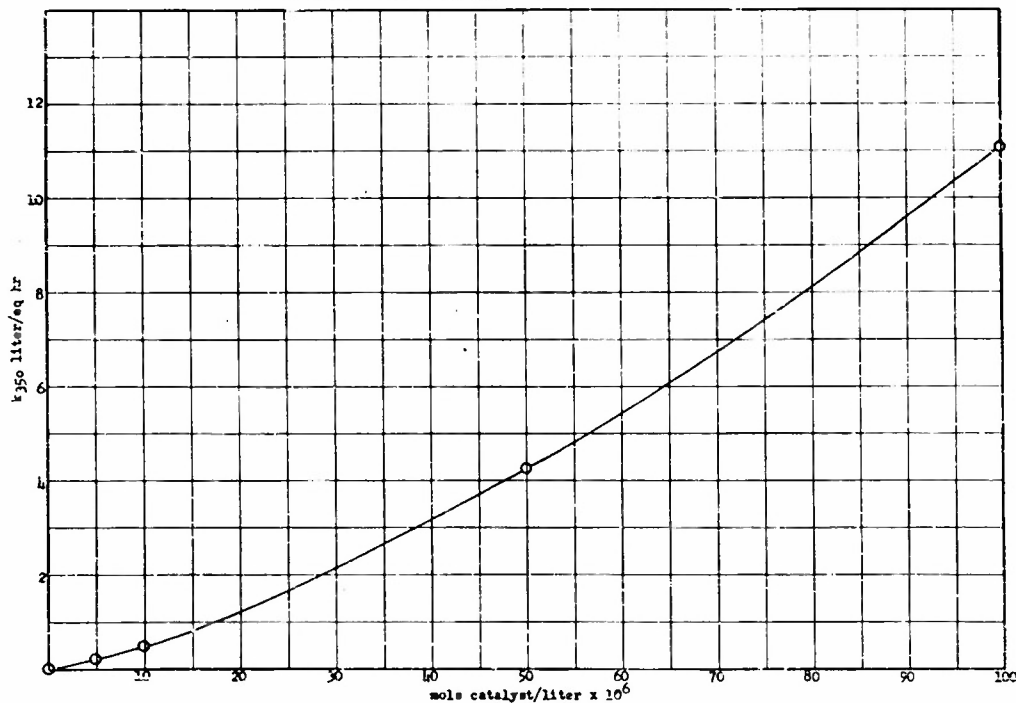


Figure 2

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II Technical Progress, B (cont.)

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TABLE II

COMPARISON OF THE CATALYTIC PROPERTIES OF METAL ACETYLACETONATES IN
POLYURETHANE I-J FORMATION

<u>Acetylacetonate</u>	<u>Rate Constant k at 50°C*</u> <u>liter/eq. hr</u>
Iron III	26
Lead II	5
Copper II	3
Manganese III	2.5
Vanadyl II	1.3
Chromium III	0.2
Nickel II	0.2
Cobalt II	0.2
Cobalt III	0.1

TABLE III

COMPARISON OF THE CATALYTIC PROPERTIES OF METAL ACETYLACETONATES
3,3-DINITRO-1,5-PENTANE DIISOCYANATE HOMOPOLYMER FORMATION

<u>Elapsed Time</u> <u>hr</u>	<u>Milliequivalents of (-NCO) Present**</u>				
	<u>Iron III</u>	<u>Lead II</u>	<u>Copper II</u>	<u>Manganese III</u>	<u>Vanadyl II</u>
0	95.0	95.0	95.0	95.0	95.0
1.0	94.7	ppt.***	91.5	91.5	94.0
2.0	—	ppt.***	91.0	89.2	93.0
20.0	—	39.6	49.0	81.2	85.0
25.0	94.6	38.6	45.2	80.2	82.5

* Initial monomer concentration, 1 eq/liter. Catalyst concentration, 1×10^{-4} mole/liter.

** Catalyst concentration 1×10^{-2} mole/liter, in dioxan solution, at 50°C. Initial (-NCO) concentration, 0.95 eq/liter.

*** Precipitated polymer prevented removal of a sample. The polymer later agglomerated, permitting sampling.

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TABLE IV

COMPARISON OF THE CATALYTIC PROPERTIES VERSUS CONCENTRATION OF
IRON III ACETYLACETONATE IN POLYURETHANE I-J FORMATION AT 35°C

Initial concentrations in dioxan solution:

0.935 eq/liter 3,3-Dinitro-1,5-pentane diisocyanate
0.935 eq/liter 2-Nitro-2-methyl-1,3-propanediol

Elapsed Time hr	No Catalyst	Degree of Polymerization			
		5 x 10 ⁻⁶ mole/liter Iron III Cat	1 x 10 ⁻⁵ mole/liter Iron III Cat	5 x 10 ⁻⁵ mole/liter Iron III Cat	1 x 10 ⁻⁴ mole/liter Iron III Cat
0	1.00	1.00	1.00	1.00	1.00
0.75	1.04	1.26	1.46	3.50	8.35
1.50	1.10	1.50	1.95	6.80	14.3
2.0	—	—	2.30	9.95	21.8
3.0	1.20	1.90	2.84	15.30	36.4
5.0	1.28	2.24	3.30	—	—
24.0	1.96	5.35	11.80	—	—
29.0	2.16	6.45	15.30	—	—
46.0	2.92	12.60	24.60	—	—
k _{35°C} liter/eq. hr = 0.047		0.26	0.55	4.3	11.1

TABLE V

RATE OF POLYURETHANE I-J FORMATION AT 50°C USING METAL ACETYLACETONATE CATALYSTS

Concentrations: 1 eq/liter (-OH) and (-NCO) in dioxan
 1 x 10⁻⁴ mole/liter metal acetylacetonate

Elapsed Time hr	Degree of Polymerization							
	$\text{Fe}(\text{C}_5\text{H}_7\text{O}_2)_3$	$\text{Pb}(\text{C}_5\text{H}_7\text{O}_2)_2$	$\text{Cu}(\text{C}_5\text{H}_7\text{O}_2)_2$	$\text{Mn}(\text{C}_5\text{H}_7\text{O}_2)_3$	$\text{VO}(\text{C}_5\text{H}_7\text{O}_2)_2$	$\text{Cr}(\text{C}_5\text{H}_7\text{O}_2)_3$	$\text{Ni}(\text{C}_5\text{H}_7\text{O}_2)_3$	$\text{Co}(\text{C}_5\text{H}_7\text{O}_2)_2$
0	1	1	1	1	1	1	1	1
0.25	8	2.2	1.7	2.0	1.3	1.1	1.1	1.1
0.75	19.5	4.8	2.8	3.4	1.9	1.2	1.1	1.1
1.50	39	9.5	5.3	4.4	2.8	1.4	1.2	1.2
19.00	—	—	—	—	—	3.5	3.8	2.5
24.00	—	—	—	—	—	4.0	5.0	3.0

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II Technical Progress, B (cont.)

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(3) Conclusions

(a) The iron III acetylacetonate is by far the best catalyst for polyurethane formation and at the same time does not catalyze the diisocyanate homopolymerization rate. Lead II and copper II acetylacetonates catalyze the diisocyanate homopolymerization. Vanadyl II and manganese III acetylacetonates have a slight effect on the homopolymerization rate. Cobalt II is more effective than cobalt III acetylacetonate. This suggests that iron II acetylacetonate should be studied.

(b) A linear relationship between catalyst concentration and rate was not obtained. Furthermore, the uncatalyzed rate at 35°C was higher than the uncatalyzed rate at 50°C reported earlier* ($k_{350} = 4.7 \times 10^{-2}$ vs $k_{500} = 2.3 \times 10^{-3}$ liter/eq hr), and the rate at 35°C using 1×10^{-5} mole/liter catalyst was lower than that reported** for the rate at 30°C ($k_{350} = 0.55$ vs $k_{300} = 1.06$ liter/eq hr). It is hoped that further studies will eliminate these discrepancies.

(4) Experimental

(a) A dioxan solution containing 1 eq/liter of each monomer was divided into 100-ml portions. To each was added the appropriate amount of recrystallized metal acetylacetonate. The solutions were maintained at 50°C and samples were periodically removed for (-NCO) determination by the standard technique***. Table V lists the observed data, and the corresponding calculated rate constants are listed in Table II.

(b) A dioxan solution containing 1 eq/liter of 3,3-dinitro-1,5-pentane diisocyanate was divided into 100-ml portions, catalysts added, then maintained at 50°C. Samples were periodically removed for (-NCO) determination***. Table III lists the observed data.

(c) A dioxan solution containing 1 eq/liter of each monomer was divided into 100-ml portions. To each was added the appropriate amount of iron III acetylacetonate. The solutions were maintained at 35°C and sampled periodically for (-NCO) determination by the standard technique.*** Table IV and Figures 1 and 2 show the observed data.

*Aerojet Report No. 590, p. 27.

**Aerojet Report No. 712, p. 7.

***Aerojet Report No. 638, p. 25.

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II Technical Progress, B (cont.)

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b. New Polyurethanes

(1) Introduction

(a) During this period, preparation of new polyurethanes of the XV series (2-nitro-2-aza-1,4-butane diisocyanate) was continued with the preparation of XV-N from ethylene glycol and XV-O from 5,5-dinitro-1,2-hexanediol. No attempts to postnitrate these polyurethanes were made, inasmuch as severe degradation occurred with XV-A (2,2-dinitro-1,3-propanediol) and XV-J (2-nitro-2-methyl-1,3-propanediol).*

(b) Limited quantities of a new nitrodiol, 3-nitro-3-aza-1,5-pentanediol, became available. It was assigned the letter P for convenience. A new polyurethane, I-P, was prepared from 3,3-dinitro-1,5-pentane diisocyanate and the new diol. Postnitration yielded polyurethane I-PN. The structures and calculated specific-impulse values are shown in Table VI.

(2) Preparation of Polyurethane XV-N from 2-Nitro-2-aza-1,4-butane Diisocyanate and Ethylene Glycol (JRF-269)

Equivalent quantities of the liquid monomers, 40 g total weight, were dissolved in 40 ml absolute dioxan. Heat was evolved, and the solution became more viscous. After 15 min, 0.011 g ferric acetylacetonate catalyst was added, resulting in further heat evolution. The mixture was maintained at 50°C for 94 hrs. The resulting viscous solution contained some solids. Dimethylformamide was used to dissolve the product, which was then precipitated by pouring into rapidly stirred ice water. The dried product weighed 39 g.

Anal. Calc'd for $C_7H_{12}N_4O_6$: %C, 33.87; %H, 4.87; %N, 22.58

Found: %C, 33.74; %H, 4.90; %N, 23.55

Heat of Combustion Calc'd: 3560 cal/g

Found: 3497 cal/g

Relative Viscosity: 1.30, 1% in dimethylformamide at 25°C.

Stability at 65.5°C, KI-Starch: >65 hr

Impact Stability: >100 cm/2 kg weight.

Softening Range: 65 to 75°C

*Aerojet Report No. 807, pp. 17 and 18.

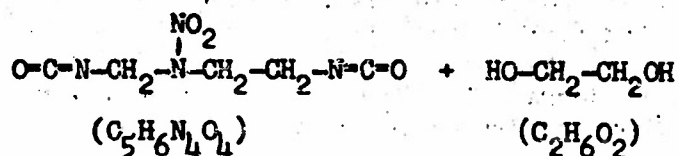
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Report No. 833

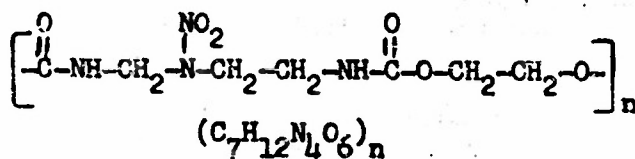
TABLE VI
NEW POLYURETHANES

Polyurethane XV-N



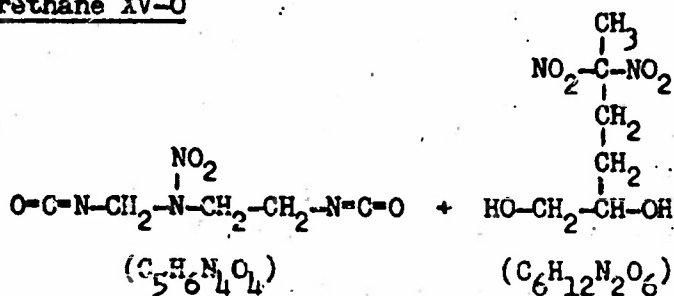
2-Nitro-2-aza-1,4-butane
Diisocyanate

Ethylene Glycol



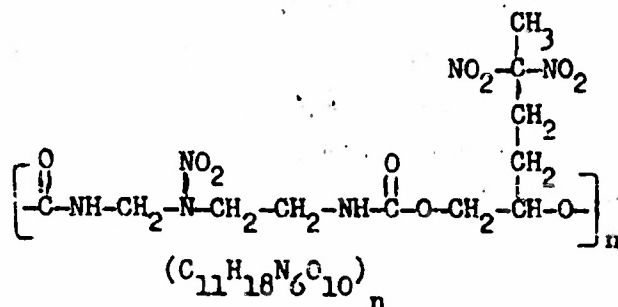
Calc'd I_{sp} = 83 lbf sec/lbm

Polyurethane XV-O



2-Nitro-2-aza-1,4-butane
Diisocyanate

5,5-Dinitro-1,2-
hexanediol

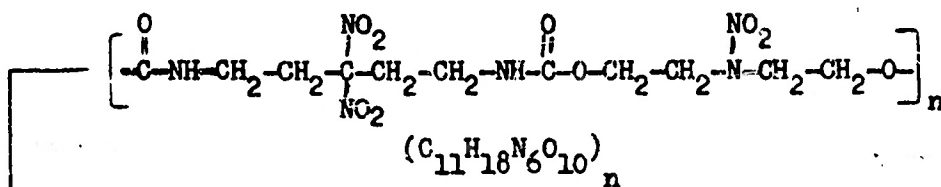
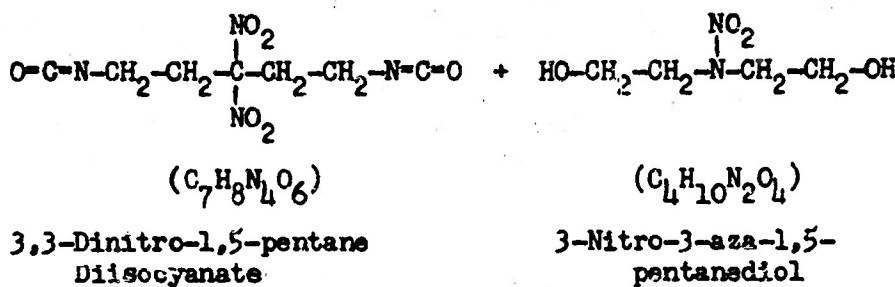


Calc'd I_{sp} = 142 lbf sec/lbm

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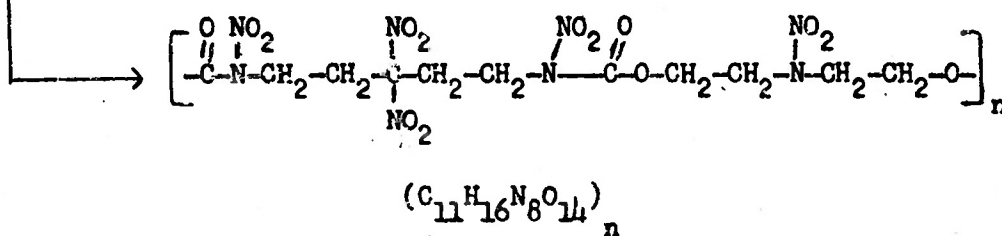
TABLE VI (cont.)

Polyurethanes I-P and I-PN



Calc'd I_{sp} = 142 lbf sec/lbm

Nitration



Calc'd I_{sp} = 207 lbf sec/lbm

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II Technical Progress, B (cont.)

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(3) Preparation of Polyurethane XV-O from 2-Nitro-2-aza-1,4-butane Diisocyanate and 5,5-Dinitro-1,2-hexanediol (JRF-270)

Equivalent quantities of the monomers, 54 g total weight, were dissolved in 54 ml absolute dioxan. Addition of ferric acetylacetonate catalyst did not result in polymerization. The red color of the catalyst was instantly changed to a light yellow by traces of acidic impurities in the diol. More catalyst was added until the red color persisted, requiring a total of 0.072 g. Heat was evolved and polymerization proceeded as usual. After 117 hr at 50°C the product was dissolved in dimethylformamide, then precipitated by pouring it into rapidly stirred ice water. The dried product weighed 52 g, and had the following characteristics:

Anal. Calc'd for $C_{11}H_{18}N_2O_{10}$: %C, 33.50; %H, 4.60; %N, 21.32

Found: %C, 33.10; %H, 4.66; %N, 21.53

Heat of Combustion Calc'd: 3643 cal/g

Found: 3571 cal/g

Relative Viscosity: 1.10, 1% in acetone; 1.13, 1% in butyrolactone; at 25°C.

Stability at 65.5°C, KI-Starch: >6.5 hr

Impact Stability: 100 cm/2 kg weight

Softening Range: 70 to 80°C

(4) Preparation of Polyurethane I-P from 3,3-Dinitro-1,5-pentane Diisocyanate and 3-Nitro-3-aza-1,5-pentanediol (JRF-268)

Equivalent quantities of the monomers, 32 g total weight, were dissolved in 32 ml of absolute dioxan. Ferric acetylacetonate, 0.0058 g, was added to catalyze polymerization. After 100 hr at 50°C the product was dissolved in acetone and precipitated by pouring into rapidly stirred ice water. The dried product weighed 31 g and had the following characteristics:

Anal. Calc'd for $C_{11}H_{18}N_2O_{10}$: %C, 33.50; %H, 4.60; %N, 21.32

Found: %C, 33.30; %H, 4.49; %N, 21.51

Heat of Combustion Calc'd: 3643 cal/g

Found: 3615 cal/g

Relative Viscosity: 1.26, 1% in acetone; 1.56, 1% in butyrolactone at 25°C.

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Stability at 65.5°C KI-Starch: 21 min

Impact Stability: >100 cm/2 kg weight

Softening range: 45-55°C

(5) Preparation of Polyurethane I-PN by Nitration of Polyurethane I-P Prepared from 3,3-Dinitro-1,5-pentane Diisocyanate and 3-Nitro-3-aza-1,5-pentanediol (JRF-275)

One hundred ml of 100% nitric acid at 0°C was added to 5 g of polyurethane I-P (JRF-268, above). After vacuum stripping excess acid at room temperature, the polymer was dissolved in acetone and precipitated by pouring the solution into methylene chloride.

Anal. Calc'd for $C_{11}H_{16}N_8O_{14}$: %C, 27.28; %H, 3.33; %N, 23.14

Found: %C, 26.78; %H, 3.46; %N, 22.70

Heat of Combustion Calc'd: 2886 cal/g

Found: 2844 cal/g

Softening range: 40 to 50°C

KI-Starch test at 65.5°C: 5 min

Impact Stability: 75 cm/2 kg

η_{sp} = 1.19, 1% in acetone at 25°C

c. Further Work on Previously Described Polyurethanes

(1) Preparation of Modified Polyurethane I-A from 3,3-Dinitro-1,5-pentane Diisocyanate, 2,2-Dinitro-1,3-propanediol, and Ethanolamine

(a) The ultimate use of Polyurethane I-A as a solid rocket propellant required some modification of the linear structure so as to yield desirable physical and mechanical properties.* It has been found that approximately 1% branching of polyurethane I-A gives improved physical and mechanical properties.** In the German "Vulcollan" rubber*** it was found that by introducing cross-links at regularly spaced intervals

*Aerojet-General Report No. 772, p. 30.

**Aerojet-General Report No. 772, p. 60.

***Bayer, Miller, Petersen, Piepenbrink and Windemuth, Zeit. Angew. Chem. 62, 57 (1950).

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of about 2500 mol wt, the tear resistance reached a maximum. The cross-linking was obtained by the reaction of diisocyanates with urea linkages, which have been reported to react 80 to 100 times as fast as urethane linkages. Petersen stated that cross-linking can occur during linear polyurethane or polyurea formation by the interaction of diisocyanate with urethane of urea linkages.*

(b) During this period, the effect on physical properties of substituting ethanolamine for a portion of the dinitropropanediol in Polyurethane I-A has been studied. Replacing one third of the dinitrodiol with ethanolamine, preparation JRF-263, gave high-molecular-weight polymer containing a small amount (<5%) of acetone-insoluble material. There was no change in the softening range. A small amount of 3,3-dinitro-1,5-pentane diisocyanate with and without ferric acetylacetonate catalyst was milled into the polymer, which was plasticized with 10 wt% dioxan. The products were soluble in acetone. After being cured for 24 hr at 80°C or 100 hr at 110°C, both uncatalyzed and catalyzed samples were insoluble in acetone. Likewise the control containing no extra diisocyanate became acetone-insoluble after further curing. It is believed that at this higher temperature the (-NCO) end groups present, due to the "dynamic equilibrium", react with the urea linkages present to give a crosslinked, acetone-insoluble product.

(c) Attempts to obtain crosslinking in solution via the urea linkage were at first unsuccessful. In the first attempt, JRF-271, an excess of diisocyanate was used to make a Polyurethane I-A of calculated DP = 32. This polymer with (-NCO) end groups was added to an equivalent amount of ethanolamine in dioxan. The portionwise addition of diisocyanate resulted at first in an increase in viscosity as precise equivalence of end groups was reached, then a decrease, indicating that little or no reaction of diisocyanate with urea linkages occurred at 50°C under the conditions used. A second attempt, JRF-272, was made, duplicating the first except that the ethanolamine was added to the Polyurethane I-A of DP = 32. The same results were observed. Later it was found that when the temperature was raised to 65°C, acetone-insoluble product was obtained in 500 hr. This indicates that the rate of reaction of (-NCO) with urea linkages is very slow at 50°C, the temperature that is normally used for the polyurethane reaction, but becomes appreciable when the temperature is raised 20 to 30°C.

(d) Experimental (JRF-263)

3,3-Dinitro-1,5-pentane diisocyanate, assay 99.0%, 20.072 g (0.0814 mole) in 30 ml absolute dioxan was added dropwise to 9.879 g (0.1617 mole) ethanolamine in 30 ml dioxan, using an ice bath to control the temperature in the range from 30 to 50°C. 2,2-Dinitro-1,3-propanediol, 53.527 g (0.3222 mole) was added; then 99.980 g (0.4054 mole) 3,3-dinitro-1,5-pentane diisocyanate in 110 ml dioxan was added dropwise, controlling the temperature in the range from 30 to 50°C with

*Ann. 562, 214 (1949).

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an ice bath. Ferric acetylacetonate catalyst, 0.068 g, was used. After 116 hr at 50°C the product was worked up in the usual manner after filtering out a small amount of acetone-insoluble product. The dried polymer softened in the range from 65 to 75°C, and a 1% solution in acetone at 25°C had a relative viscosity of 2.49.

(e) Experimental (JRF-271)

A solution of 41.00 g (0.330 eq.) 3,3-dinitro-1,5-dinitro-1,5-pentane diisocyanate in 50 ml dioxan was added dropwise to a slurry of 25.810 g (0.310 eq.) 2,2-dinitro-1,3-propanediol in 17 ml dioxan plus 0.022 g ferric acetylacetonate catalyst. The temperature was maintained at 50°C for 2 hr, and the polymer solution was then added slowly to a solution of 1.110 g (0.0182 mole) ethanolamine in 15 ml dioxan. A small amount of heat was evolved, but the viscosity remained constant. More diisocyanate, 2.00 g (0.0164 eq.) was added to give calculated equivalence of end groups. The solution was then maintained at 50°C. Table VII shows the observed solution and relative viscosities.

(f) Experimental (JRF-272)

The above experiment was duplicated except that the ethanolamine was added to the polymer.

(2) Preparation of Modified Polyurethane I-A from 3,3-Dinitro-1,5-pentane Diisocyanate, 2,2-Dinitro-1,3-propanediol, and Water

(a) Earlier studies have shown that nitro-polyureas can be prepared from nitrodiisocyanates and water.* The use of ethanolamine to introduce urea linkages in Polyurethane I-A lowers the specific impulse of the polymer. By using water to produce 3,3-dinitro-1,5-pentane diamine in situ, this loss of specific impulse is reduced.

(b) Polyurethane I-A of calculated DP = 32 having (-NCO) end groups was prepared in 50% dioxan solution. Urea formation and chain lengthening was achieved by adding sufficient water to react with one-half the (-NCO) end groups, yielding amine end groups which reacted with the remainder of the (-NCO). The addition of 3,3-dinitro-1,5-pentane diisocyanate resulted in acetone-insoluble product after 140 hr at 65°C. This is a much shorter time than was required for crosslinking at 65°C using ethanolamine (see above). It is believed that some branching occurred when water was added to the polyurethane I-A DP = 32, thus requiring fewer bonds for complete insolubility. Such branching and crosslinking was observed when polyureas were prepared from diisocyanates and water.**

(c) Experimental (JRF-273)

A solution of 41.00 g (0.330 eq.) 3,3-dinitro-1,5-pentane diisocyanate in 50 ml dioxan was added dropwise to a slurry of 25.81 g (0.310 eq.) 2,2-dinitro-1,3-propanediol and 0.011 g

*Aerojet Report No. 74C, p. 30.

**Aerojet Report No. 74D, p. 30; also O. Bayer, Zeit. Angew. Chem. 59, 257 (1947).

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TABLE VII

MODIFIED POLYURETHANE I-A, JRF-271. SOLUTION AND RELATIVE VISCOSITIES

<u>Elapsed time at 50°C</u>	<u>Solution Viscosity</u>	<u>η_r 1% acetone</u>	<u>Remarks</u>
0 hr	1.6 sec	—	
2	1.6	1.20	Added to ethanolamine
2.5	1.6	1.13	Added 2.00 g diisocyanate
20.0	10.0	1.30	
24.0	14.2	—	Added 0.184 g diisocyanate
26.5	39.0	—	Added 0.138 g diisocyanate
27.5	50.0	—	
92.0	125.0	1.56	Added 2.55 g diisocyanate
96.0	94.0	1.58	
99.0	68.0	—	
116.0	49.0	—	
120.0	35.0	1.50	Added 1.050 g diol
141.0	60.0	—	Added 0.235 g diol
147.0	51.0	—	Added 0.486 g diisocyanate
165.0	66.0	1.43	

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ferric acetylacetonate in 10 ml dioxan. The temperature was maintained at 50°C for 1 hr, and a solution of 0.180 g (0.01 eq.) water in 7 ml dioxan was added. After 24 hr at 65°C, 1.25 g (0.01 eq.) 3,3-dinitro-1,5-pentane diisocyanate was added. The solution viscosity dropped at first from 22 sec efflux to 13 sec. After 50 hr at 65°C there was a steady rise to 95 sec efflux after 125 hr, the solution reaching insolubility after 140 hr at 65°C.

2. New Polyureas - Preparation of Polyurea XV-C from 2-Nitro-2-aza-1,4-butane Diisocyanate and Water

a. Using the technique of preparing the diamine in situ from diisocyanate and water* a new polyurea of the XV series was prepared (see Table VIII for structure and estimated specific impulse.)

b. To a 500-ml resin flask containing 2.043 g (113 meq) distilled water in 10 ml absolute dimethylformamide was added portionwise 21.645 g (227 meq) of diisocyanate (assay 97.5%) in 15 ml dimethylformamide. Immediate heating and gassing were observed in the reaction solution. After all the diisocyanate was added the temperature was maintained at 65°C for 114 hr. The viscous solution was diluted with DMF, then poured into rapidly stirred ice water. The precipitated polymer was collected and dried.

Anal. Calc'd for $C_8H_{16}N_8O_6$: %C, 30.00; %H, 5.04; %N, 34.99

Found: %C, 31.28; %H, 4.72; %N, 35.09

Heat of Combustion Calc'd: 3730 cal/g

Found: 3690 cal/g

Softening Range: 155 to 160°C

KI Starch test at 65.5°C: >5 hr

Impact Stability: >100 cm/2 kg

$\eta_r = 1.07$ (1% in dimethylformamide at 25°C).

*Aerojet Report No. 740, p. 30.

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II Technical Progress, B (cont.)

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ferric acetylacetonate in 10 ml dioxan. The temperature was maintained at 50°C for 1 hr, and a solution of 0.180 g (0.01 eq.) water in 7 ml dioxan was added. After 24 hr at 65°C, 1.25 g (0.01 eq.) 3,3-dinitro-1,5-pentane diisocyanate was added. The solution viscosity dropped at first from 22 sec efflux to 13 sec. After 50 hr at 65°C there was a steady rise to 95 sec efflux after 125 hr, the solution reaching insolubility after 140 hr at 65°C.

2. New Polyureas - Preparation of Polyurea XV-E from 2-Nitro-2-aza-1,4-butane Diisocyanate and Water

a. Using the technique of preparing the diamine in situ from diisocyanate and water* a new polyurea of the XV series was prepared (see Table VIII for structure and estimated specific impulse.)

b. To a 500-ml resin flask containing 2.043 g (113 meq) distilled water in 10 ml absolute dimethylformamide was added portionwise 21.645 g (227 meq) of diisocyanate (assay 97.5%) in 15 ml dimethylformamide. Immediate heating and gassing were observed in the reaction solution. After all the diisocyanate was added the temperature was maintained at 65°C for 114 hr. The viscous solution was diluted with DMF, then poured into rapidly stirred ice water. The precipitated polymer was collected and dried.

Anal. Calc'd for $C_8H_{16}N_8O_6$: %C, 30.00; %H, 5.04; %N, 34.99

Found: %C, 31.28; %H, 4.72; %N, 35.09

Heat of Combustion Calc'd: 3730 cal/g

Found: 3690 cal/g

Softening Range: 155 to 160°C

KI Starch test at 65.5°C: >5 hr

Impact Stability: >100 cm/2 kg

$\eta_r = 1.07$ (1% in dimethylformamide at 25°C).

*Aerojet Report No. 740, p. 30.

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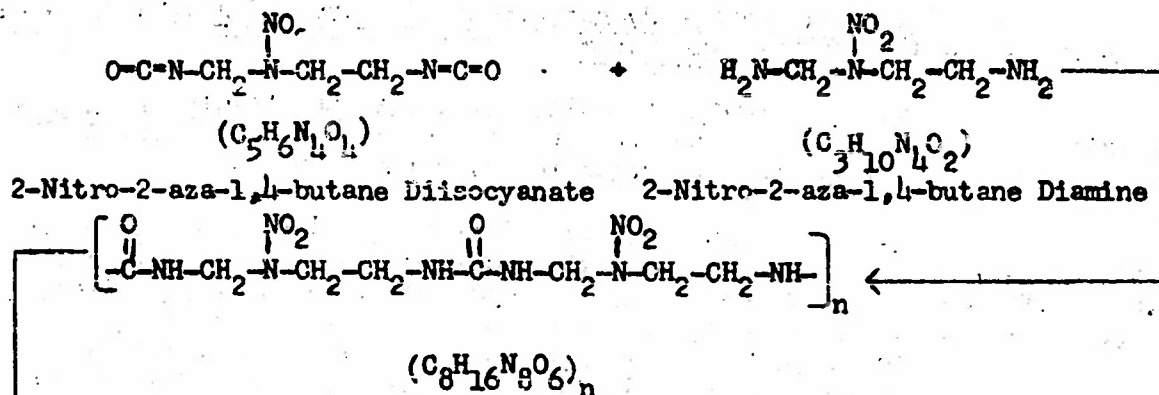
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TABLE VIII

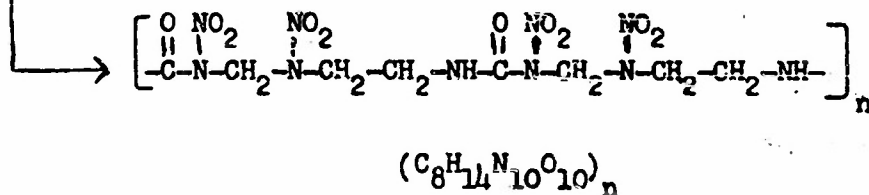
NEW POLYUREAS

Polyureas XV- ξ and XV- ξ N



Theoretical $I_{sp} = 152 \text{ lbf sec/lbm}$

Nitration



Theoretical $I_{sp} = 211 \text{ lbf sec/lbm}$

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III. TECHNICAL PROGRESS: FORMULATION STUDIES

A. INTRODUCTION

Mechanical-properties studies on linear nitropolymers have revealed that these polymers will not have the strength necessary to withstand the stresses and strains which will occur during firing of a nitro-polymer grain. As a result, a great deal of effort has been expended in improving the physical properties of nitropolymers by the introduction of branching and crosslinks. During the past quarter, formulation studies directed toward developing a nitropolymer grain have continued with further investigations of polyurethane systems modified with plasticizers and crosslinking agents. In particular, casting studies including systems containing inorganic oxidizers have been made. These formulated products were characterized by determinations of burning rates, pressure exponents, thermal stabilities, and impact stabilities. A number of non-nitro plasticizers have been investigated with respect to polyurethane compatibility and utility in oxidizer-filled formulations. Two new nitroplasticizers, 1,3,3-trinitro-butane and methyl 4-nitrazavalerate, have been utilized in one-stage castings based on a polyurethane system. Finally, second-stage crosslinking in polyurethane-based systems has been studied with the purpose of obtaining practical curing reactions in order to add structural strength to otherwise thermoplastic propellant formulations.

B. CASTING STUDIES

1. Discussion

The previously described one-stage casting techniques* have been applied to the Polyurethane XIII-A system using dioxan, methyl 4,4-dinitrovalerate, methyl 4-nitrazavalerate, and 1,3,3-trinitrobutane as plasticizers. Three-eighths to 1/2-in. rods were produced in test-tube molds. During the past quarter flat-bottomed crystallizing dishes were used as molds for these castings, and in most cases, uniform flat sheets were obtained. Experimental data given in Table IX show that runs No. 256, 260, and 261 did not yield the expected gel, such as was obtained when dioxan or MDNV was used in earlier compositions.** However, when freshly distilled MDNV was used (Run No. 262) the expected gel formation gave rise to opaque castings. When MDNV was freed of any acid impurities and distilled, the clear gelled product was found superior to the previous formulations.

*Aerojet Report No. 807, p. 29.

**Aerojet Report No. 809, p. 33.

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TABLE IX

POLYURETHANE XIII-A CASTINGS

Run	Solvent	Solvent Conc. (wt.%)	Triol Conc. (eq.%)	Cat. Conc. moles FeAA/eq. NCO	Cure	Results
254	Dioxan	30	10	2×10^{-5}	30 hr at 110°F	Soft gel, cracked on cooling
255	Dioxan	15	2	2×10^{-5}	16 hr at 110°F	Hard gel, few bubbles
256	MDNV ¹	50	2	1×10^{-5}	4 days at 110°F	No gel
260	MDNV ¹	35	2	4×10^{-5}	60 hr at 50°C	No gel
261	MDNV ¹	35	10	3×10^{-5}	20 hr at 110°F	Soft, rubbery gel
262	MDNV ²	35	10	2×10^{-5}	16 hr at 110°F	Opaque, bubble-free gel
263	NDNV ³	35	10	2×10^{-5}	16 hr at 110°F	Opaque, bubble-free gel
264	TNB ⁴	35	10	2×10^{-5}	16 hr at 110°F	No gel, bubbles
283	NDNV ⁵	35	2	3×10^{-5}	16 hr at 110°F	Soft, rubbery gel
284	MNV ⁶	30	2	3×10^{-5}	6 days at 110°F	Weak, bubble-filled gel

¹Methyl 4,4-dinitrovalerate, batch 1, distilled several months ago. Previously gave good gels.

²Batch 2, freshly distilled.

³Batch 2 treated with activated alumina.

⁴1,3,3-Trinitrobutane.

⁵Batch 3, carbonate treated, freshly distilled.

⁶Methyl 4-nitrazavalerate.

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2. Conclusions

The extremely sensitive nature of the monomers in these systems, particularly the diisocyanates, demands the ultimate in plasticizer purity. It is seen that when methyl 4,4-dinitrovalerate is kept for several months, even at 0 to 5°C, small amounts of decomposition impurities are sufficient to prevent complete gelation at a 10% crosslinking level. The trinitrobutane and methyl 4-nitrazavalerate plasticizers also show acidic impurities which lead to bubble formation and prevent complete gelation. Future work will show whether these nitroplasticizers can also be freed of these inhibiting impurities.

C. INORGANIC OXIDIZER FORMULATIONS

1. It has been reported that nitropolymers could not be extruded because of unusually high cohesive forces.* However, in combination with inorganic salts or oxidizers successful extrusions were conducted. These specimens showed a high burning rate and appeared to be of interest in special applications such as igniter materials.

2. As a result, several new formulations containing XIII-A (27%)-TNB (12%)- NH_4ClO_4 (60%)- $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ (1%) were prepared and tested as igniter material (Runs 257, 258, 259, 265, Table X). It was found in these tests that the burning rate was too low for igniters and ignition delays greater than specifications allowed were observed.

3. Several new compositions containing inorganic oxidizers were prepared in order to obtain information on burning-rate modifiers in nitro-polyurethane binder systems (Table X). The Warburg stability tests of two formulations containing TNB show a high rate of gassing. It was found that this high gassing rate was due to impurities in the TNB. Vigorous purification of subsequent batches of TNB yielded a product which did not gas at a measurable rate in the Warburg test.

D. SECOND-STAGE CROSSLINKING STUDIES

1. Discussion

a. When crosslinked polyurethanes (containing 1 to 2% crosslinks) are used in inorganic oxidizer formulation, it has been found that during the milling operations the polymer degraded sufficiently to become soluble and hence thermoplastic. Therefore, reestablishment of the tridimensional structure in the final grain is desirable. In an attempt

*Aerojet Report No. 809, p. 37.

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TABLE X
NITROPOLYURETHANE-OXIDIZER EXTRUSIONS

Run	Formulation		Wt Prep. Calc'd (gms) (psi)	Extrusion Temp (°F)	Pressure (psi)	Burning Rate (in/sec at 1000 psi, 60°F)	Warburg ² Stability (ml/100g/hr) Exp. (at 65.5°C)	Impact Stab. (cm/2 kg)
	Polymer Plast.	Oxidizer						
257	XIII-A (27%)	TNB ¹ (12%) NH ₄ ClO ₄ (60%)	(NH ₄) ₂ Cr ₂ O ₇ (1%)	150	248	125	15000	
258	XIII-A (27%)	TNB ¹ (12%) NH ₄ ClO ₄ (60%)	(NH ₄) ₂ Cr ₂ O ₇ (1%)	120	248	125	15000	
259	XIII-A (27%)	TNB ¹ (12%) NH ₄ ClO ₄ (60%)	(NH ₄) ₂ Cr ₂ O ₇ (1%)	280	248	125	15000	
265	XIII-A (27%)	TNB ¹ (12%) NH ₄ ClO ₄ (60%)	(NH ₄) ₂ Cr ₂ O ₇ (1%)	40	248	—	—	40
266	XIII-A (10%)	TNB (10%) NH ₄ ClO ₄ (60%)	XIII-AN (20%)	50	253	—	—	40
267	XIII-A (27%)	TNB (12%) NH ₄ ClO ₄ (60%)	(NH ₄) ₂ Cr ₂ O ₇ (1%)	40	248	110	20000	40
268	XIII-A (17%)	TNB (8%) NH ₄ NO ₃ (75%)	—	50	235	130	20000	>100
269	XIII-A (17%)	TNB (8%) NH ₄ NO ₃ (73%)	(NH ₄) ₂ Cr ₂ O ₇ (2%)	50	235	110	20000	>100
289	XIII-A (28%)	TNB (12%) NH ₄ ClO ₄ (56%)	NaN ₃ (1%)	50	—	105	15000	—

- 1 1,3,3-Trinitrobutane
2 TNB alone gases at a rate of 1.0 ml/100 g/hr at 65.5°C
3 Sodium dinitroacetone trile

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III Technical Progress, D (cont.)

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to crosslink the thermoplastic oxidizer-containing formulations, a number of potential crosslinking agents and catalysts have been investigated. Straight-chained, branched-soluble (0.5% triol), crosslinked-insoluble ($\geq 1\%$ triol), and urea-containing polyurethanes have been studied under a variety of conditions. From these experiments the following conclusions have been drawn: (1) the only crosslinking observed was obtained when a linear or branched-soluble system was maintained at an elevated temperature; (2) crosslinking did not occur in the presence of any plasticizers; (3) various forms of formaldehyde and glyoxal showed no tendency to crosslink with the polyurethane.

b. Studies made on Polyurethane I-A modified with 33% ethanolamine have indicated that the soluble polymer could be made insoluble by heating for 24 hr at 180°F both in the presence and absence of diisocyanate monomer (see this report, p.21.) It was thought that this reaction might be of interest as a curing reaction in a composite system containing this modified polyurethane. Accordingly, compositions of this polyurethane and ammonium nitrate were formulated in the presence of various solvents and plasticizers and cured at 180°F. Table XI shows the results of these experiments.

TABLE XI

MODIFIED I-A--AMMONIUM NITRATE FORMULATIONS

Run	Composition, wt%			Solvent or Plasticizer	Cure (hr at 180°F)	Results (Solubility in)
	Polymer	Plasticizer	NH ₄ NO ₃			(Aqueous Acetone)
271	17	8	75	Dioxan	16	Partly insoluble
271-1	17	8	75	Dioxan	72	Insoluble
272	17	8	75	MDNV ¹	72	No gel
273	17	8	75	Triacetin	36	No gel
274	20	5	75	Triacetin	16	No gel

¹Methyl 4,4-dinitrovalerate

c. The literature reports that bases catalyze the reaction of isocyanates with urea hydrogens. The following compounds were added to an acetone solution of the urea-modified polyurethane I-A: dimethylformamide, activated alumina, pyridine, urea, p-nitro-N-methylaniline, dimethylaniline.

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No gels were obtained upon curing for 16 hr at 180°F, including the control solution. A control solution from which all the solvent was allowed to evaporate was found to produce an acetone-insoluble product.

d. Studies on linear and branched soluble polyurethanes also showed the same characteristics as the urea-modified polymer. Polyurethanes I-A and XIII-A which were made with 0.5% nib-glycerol and which were both acetone-soluble became insoluble when heated 16 hr at 80°C or 1 hr at 100°C. Linear soluble Polyurethanes I-A and XIII-A became insoluble upon heating at 150°C for 15 min. However, when any solvent or plasticizer was added no gels were obtained on continued heating at elevated temperatures.

e. Crosslinking reactions were also attempted with formaldehyde and glyoxal. No gels were obtained when formalin, nib-glycerol, glyoxal-water and glyoxal-dioxan were added to acetone solutions of Polyurethane I-A (straight and urea-modified) and cured overnight at 180°F.

2. Conclusions

It is known that most addition products of isocyanates dissociate at elevated temperature, giving their free, reactive, monomeric end groups. The temperature at which this dissociation takes place is known as the "abspalter" temperature, and is characteristic of each addition compound.* It is believed that the nitropolyurethanes are also exhibiting "abspalter" properties; and at elevated temperatures, rearrangement and/or decomposition reactions are leading to crosslinking via the urethane or urea hydrogens. Any diluents slow these rearrangement rates to the extent of preventing a gel before decomposition occurs. Furthermore, plasticizers containing acids, water, or other isocyanate-reactive materials cannot be used in "abspalter" reactions involving the urethane grouping.

E. FORMULATION WITH COMMERCIAL PLASTICIZERS

1. Two of the plasticizers compatible with polyurethane I-A, dibutyl phthalate and tricresyl phosphate, were used in formulations containing ammonium nitrate. In both cases, the strong, rubbery, well-plasticized polymer binder lost strength and began to crumble as soon as the first of the oxidizer salt was added. It is concluded that possibly the phenyl groups in these plasticizers are too bulky and non-polar to allow efficient plasticization after the highly polar salt is added.

* Petersen, Ann. 562, 219 (1949).

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IV. TECHNICAL ADDRESS: MANUFACTURING OF NITROPOLYMERS

A. INTRODUCTION

1. One factor of great importance in future application of nitropolymers is the cost of manufacture of nitromonomers and their polymerization products. This is radically affected by the nature of the processing equipment and operations. In the production of monomers, it is expected that the scale-up will follow the normal course of operation in conventional equipment. Here problems of obtaining monomers of the required purity will increase with the quantity produced. Another problem will be the development of processes suitable for performance in hardware involving a minimum of transfers. These problems will be approached in larger pilot plant runs.

2. The preparation of nitropolymers, however, will require greater attention and study on a laboratory scale before any scale-up can be made. Some time ago a Beken dispersion blade mixer was installed, and this piece of equipment allows the polymerization mixtures to be studied under conditions comparable to those encountered during actual manufacture.* Experience gained in the Beken mixer operations will provide necessary data for the scale-up into large plant-size equipment.

B. POLYURETHANES

1. Discussion

a. The manufacture of nitropolyurethanes deals with several problems which are not encountered or are of small importance in laboratory size experiments:

(1) Dissipation of heat of reaction — This is of great importance, because the formation of the urethane linkage liberates 52 kcal per mole

(2) Polymer concentration in the mixture in a homogeneous or heterogeneous medium

(3) The time required to bring a batch to the desired molecular weight

(4) The reproducibility and uniformity of the products obtained

(5) The exclusion of side reactions caused by the extreme reactivity of the monomers with chemicals such as water

*Aerojet Report 772, Appendix A; No. 807, p. 23.

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(6) The method of isolation of the polymer

(7) The cost and economy of manufacture under various conditions

During the past two months several polyurethane runs have been conducted, and some of the problems were studied. In every instance laboratory pilot runs of the monomers were carried out prior to runs on the large batch in order to check monomer equivalence. The larger master batch was then started with adjusted monomer equivalence. The monomers were mixed in the conventional way, and catalyst was present from the start.

b. When the polymerization was conducted in a homogeneous single phase, using dioxan as a solvent, the production time could be held to a minimum, and a batch was completed within a day's time and in most cases in less than five hours. The work-up of the polymers has been accomplished by three methods: (1) precipitating a dioxan-acetone solution of the polymer into water, using the Morehouse mill, (2) driving off reaction solvent using a roller mill, and (3) grinding the polymer in an inert reaction solvent and filtering off solvent. The first of these is more time-consuming and entails a drying operation which is eliminated by the second method. However, using the Morehouse mill, a pure fibrous product is obtained which can be readily used for formulation studies. By use of the roller mill it is very difficult to remove all of the solvent. In the case of formulation studies using a solvent-plasticizer system this method would be of advantage. The third method still requires study, but it involves preliminary polymerization in a homogeneous solvent followed by precipitation in the mixer with an inert non-solvent such as a hydrocarbon.

c. The use of benzene as a polymerization medium has been investigated. If the polymerization can be controlled it would be by far the most favorable procedure. It has been found that the polymer produced was a dense, granular product which could be filtered directly from the reaction mixture. However, several batches failed because of mechanical difficulties, giving a product which had unfavorable physical characteristics. It was believed that by using benzene as a solvent the heat of reaction and/or the heat of mixing could easily be kept below the boiling point of benzene. However, in two cases the boiling of the benzene caused swelling of the polymer and extrusion through the port of the mixer. One case resulted in a small flash fire which destroyed the batch.

d. Reproducibility and uniformity are being checked with physical measurements and stability tests of the final product. However, in order to obtain a high-molecular-weight, reproducible product a method must be developed to follow the course of the polymerization. Various methods have been tried but were either unsuccessful or not

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IV Technical Progress, B (cont.)

applicable to the Aerojet process. The most feasible method tried seems to be a solution viscosity taken with a dilute sample lifted during the polymerization. This should be a fast and inexpensive method, but in one attempt the results were not reproducible. Further work will be done to develop this method. In the experimental section a representative nitro-polyurethane run in the Beken mixer is discussed. Table XII summarizes the batches, showing the differences in operating conditions and work-up procedures.

2. Experimental

a. Polyurethane XIII-J Obtained from 3-Nitro-1,5-pentane Diisocyanate and 2-Nitro-2-methyl-1,3-propanediol and 0.5% tris-Hydroxymethyl Nitromethane in the Beken Mixer

(1) Experimental (RDH-23)

A solution of 490.155 g 3-nitro-1,5-pentane diisocyanate (assay 97.39%) in 619 ml of absolute dioxane was slowly added to a slurry of 326.770 g 2-nitro-2-methyl-1,3-propanediol, 1.2013 g tris-hydroxymethyl nitromethane, and 0.3362 g ferric acetylacetonate in 200 ml of absolute dioxane. The temperature of the reaction mixture during the diisocyanate addition was held between 35 and 50°C by means of the heat exchange system and adjustment of the rate of addition. The addition time was 3 hr. The ultimate monomer concentration was 50 wt% with a calculated excess of 1.41% diol. The reaction mixture was then kept at 50°C by means of the heat exchange system. After 3 hr of mixing, a sample was withdrawn and found to be very viscous and on the verge of insolubility. The very viscous polymer was next removed from the mixer and worked on a heated roller mill for 2.5 hr. A sheet of very tough but pliable polymer was obtained which had a solvent concentration of 50 wt%.

b. A summary of polyurethane runs in Beken mixer is compiled in Table XII.

TABLE XII
SUMMARY OF POLYURETHANE RUNS IN BEKEN MIXER

Run No.	Type Polymer	Branching Agent % by wt.	Solvent Type	Concn.	Addition Time hr.	Mix Time hr.	Temp. °C	Work-up Procedure	Relative Viscosity 1% in Acetone	Marburg Stability ml. 40% TOL. g./hr.	EL-Starch Stability min to failure	Remarks
RDH-1	Polyurethane I-A ¹	0.5% NO ²	Dioxan	25%	1.5	72	50	Ppt into Marehouse mill	Insoluble	.09	60	White, fluffy insoluble polymer when dry - used for nitrations
RDH-18	Polyurethane XIII-A ²	0.5% NO	Dioxan	50%	2.5	21.5	50	Ppt into Marehouse mill	2.15	.002	120	Used for formulation studies
RDH-20	Polyurethane XIII-B ³	0.5% NO	Dioxan	50%	2.5	5.0	50	Heated roller mill	Insoluble	.12	>150	Very tough but workable sheet of polymer - no odor of solvent
RDH-23	Polyurethane XIII-J	0.5% NO	Dioxan	50%	3.0	3.0	50	Heated roller mill	Insoluble	.12	>180	Polymer was soluble in acetone before work-up on roller mill
RDH-27	Polyurethane I-A	--	Dioxan	20%	2.5	7.0	50-67	Ground in Beken mixer and Marehouse mill	Insoluble	.15	40	Polymer gelled and was partially ground in Beken mixer - ground finer in Marehouse mill
RDH-29	Polyurethane I-A	--	Benzene	50%	2.5	5.75	50-70	Ground in Beken mixer	1.12	.08	50	Polymer was very dense and brittle - work-up procedure very simple and fast
RDH-33	Polyurethane XIII-A	--	Benzene	50%	2.5	5.0	5-78	Ground in Beken mixer	Insoluble	1.3	21	Polymer swelled in Beken mixer and extruded through the top port of the mixer
RDH-34	Polyurethane XIII-A	--	Benzene	65%	6.0	6.0	60-7	--	--	--	--	While mixing the temp rose to 65°C - cool cycle on - polymer started extruding thru port - small flash fire destroyed batch

¹ Polyurethane I-A is 2,2-dinitro-1,3-propanediol + 3,3-dinitro-1,5-pentane diisocyanate

² Polyurethane XIII-A is 2,2-dinitro-1,3-propanediol + 3-nitro-1,5-pentane diisocyanate

³ Polyurethane XIII-J is 2-nitro-2-methyl-3-propanediol + 3-nitro-1,5-pentane diisocyanate

40 is Nib-glycerol.

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3. Conclusions

Polyurethanes produced in the Beken mixer at 50°C using dioxan as a solvent have been produced successfully in monomer concentrations of up to 70 wt%. However, when the monomer concentration was increased to 80 wt% an insoluble gel was obtained, probably because of the inability to dissipate the heat of reaction and keep the temperature under control. When benzene was used as a combination solvent and heat-exchange medium, the runs were unsuccessful, but a modification of the procedure might give favorable results. The high density of the polymer appears to be very attractive. Stability tests on all runs were consistent. This indicates that the runs are reproducible.

V. TECHNICAL PROGRESS: PHYSICAL STUDIES

A. INTRODUCTION

The osmometric molecular-weight determinations on polyurethanes have been studied in the past, and the relationship between intrinsic viscosity and number average molecular weight has been established. During the past quarter a similar osmometric molecular-weight study of poly-2,2-dinitrobutyl acrylate has been made.

B. OSMOMETRIC MOLECULAR WEIGHT OF POLY 2,2-DINITROPROPYL ACRYLATE

1. The preparation of a series of poly-2,2-dinitrobutyl acrylate samples under various conditions of polymerization temperature and initiator concentration was described previously.* Molecular-weight determinations have been made on the preparations, the results of which are shown in Table XIII. The errors, listed in the sixth column, were determined from the mean square deviations of the π/c vs c plots, assuming all the error to be in the determination of π/c .

2. A plot of log molecular weight vs log intrinsic viscosity is shown in Figure 3. The errors shown in Table XIII are indicated approximately by the diameter of the circles in Figure 3. The plot shows that the preparation of highest molecular weight (DNBA 57) deviates radically from the line formed by the other five. Two solutions for the best linear plot by the method of least squares are shown, one including all six points, the other omitting preparation DNBA 57. A calculation for the constants in the Staudinger equation ($[\eta] = KM^a$) gives the following:

	<u>K</u>	<u>a</u>
Six-point solution	1.22×10^{-3}	0.505
Five-point solution	1.92×10^{-5}	0.840

*Aerojet Report No. 740, pp. 6-7.

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TABLE XIII

MOLECULAR WEIGHTS, POLY-2,2-DINITROBUTYL ACRYLATE

Preparation	Initiator,* mole/liter	Polymerization Temperature, °C	Intrinsic Viscosity, [η]	M_n	Error
DNBA 57	0.01	40	1.160	1,070,000	+50,000 -45,000
DNBA 54	0.1	40	1.073	469,000	+20,000 -18,000
DNBA 56	0.01	50	0.866	339,000	+7400 -7100
DNBA 53	0.1	50	0.721	239,000	+7100 -6700
DNBA 55	0.01	60	0.574	230,000	+6700 -6300
DNBA 52	0.1	60	0.439	163,000	+4100 -3900

An inspection of a compilation of Staudinger equation constants for various polymer-solvent systems** shows that the values obtained in the six-point solution are near the extreme limits of the range of values in the compilation. The five-point solution, on the other hand, gives normal values for the constants. It is especially noteworthy that the value of 0.505 from the six-point solution is near the theoretical limit of 0.500.

3. It is concluded that the five-point solution, with values for K and a of 1.92×10^{-5} and 0.840 respectively, probably gives a more nearly correct relationship between intrinsic viscosity and molecular weight for poly-2,2-dinitrobutyl acrylate. A reference curve on a log-log plot is shown in Figure 4, from which the intrinsic viscosities and molecular weights may be read directly. Determination of molecular weights greater than 500,000 are very difficult with the osmometric method, because the osmotic pressures are so low that they cannot be measured with good precision at low concentrations. Accordingly, it is concluded that the value of 1,070,000 for DNBA 57 is erroneous, and that the good agreement of the points in the η/c vs c plot for this preparation was fortuitous.

* Azo-bis-isobutyronitrile

** H. Mark and A. V. Tobolsky, Physical Chemistry of High Polymeric Systems, Interscience Publishers, New York, 2nd Ed, 1950, p. 290.

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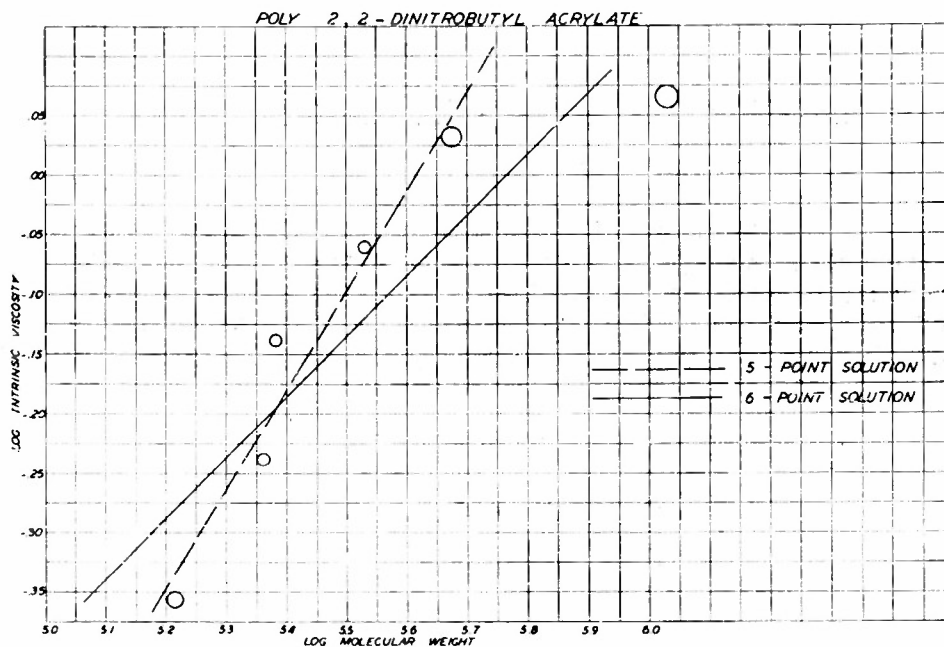


Figure 3

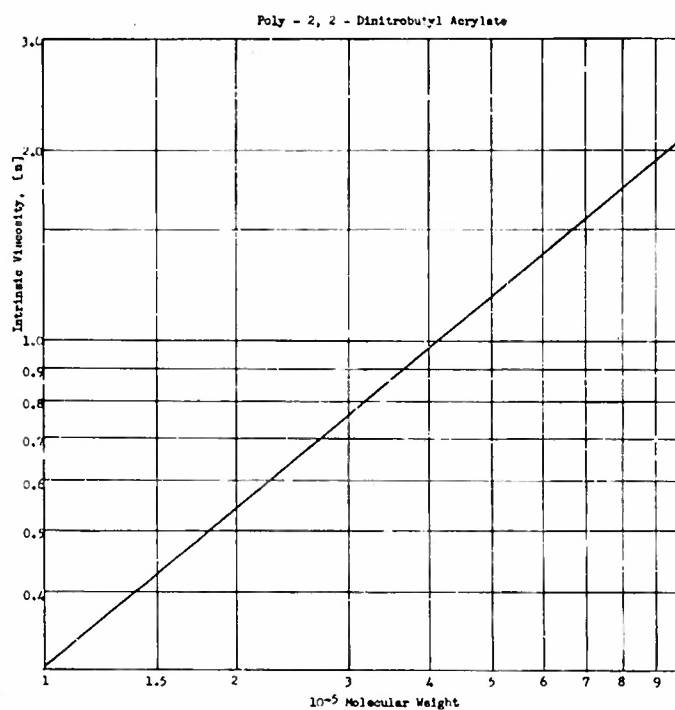


Figure 4

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VI. TECHNICAL PROGRESS: ORGANIC SYNTHESIS

A. INTRODUCTION

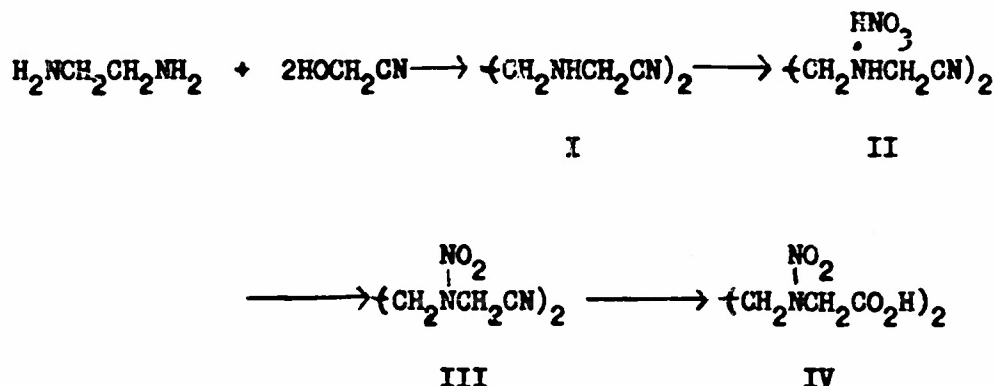
Diisocyanates containing the nitramino group are particularly interesting among the nitromonomers suitable for polyurethane formation because of the readily available starting materials and the simplicity of introduction of the energy-donating nitro groups. During the past quarter several nitramino dicarboxylic acids have been prepared and converted into the corresponding diisocyanates.

B. NITRO DICARBOXYLIC ACIDS

1. Preparation of 3,6-Dinitraza-1,8-octanedioic Acid

a. Discussion

3,6-Dinitraza-1,8-octanedioic acid, a new dicarboxylic acid containing two nitramino groups, was prepared by the following sequence of reactions:



N,N'-Ethylene diglycine or 3,6-diaza-1,8-octane dinitrile (I) has been obtained previously by a Mannich condensation of ethylene diamine, hydrogen cyanide, and formaldehyde in aqueous solution in the presence of an alkaline-earth cyanide.* In our synthesis of this material, the condensation was effected using the commercially available aqueous glycolonitrile in the absence of any inorganic catalyst. The condensation product was not isolated but converted to the bis nitric salt (II) in aqueous solution. All of the intermediates in this particular series were relatively more unstable to heat (all melting with decomposition) than the corresponding intermediates containing more than one methylene group between the nitramino group and the functional group. However, the nitric acid salt appeared to be the most unstable, since considerable decomposition occurred during an initial

* Pick and Ulrich, German Pat. 638,071, Nov. 9, 1936.

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recrystallization of this material from hot water. The conversion of the nitric acid salt to 3,6-dinitraza-1,8-octane dinitrile (III) was effected by a chloride-catalyzed nitration, and the hydrolysis of this nitrile was carried out in concentrated hydrochloric acid to yield 3,6-dinitraza-1,8-octanedioic acid (IV). The dinitrile and dicarboxylic acid were obtained in 71 and 63% yields, respectively. Both compounds exhibited high melting points.

b. Experimental

(1) Preparation of the Bis Nitric Acid Salt of 3,6-Diaza-1,8-octane Dinitrile

To 81.7 g (1.04 moles) 76.5% aqueous ethylene diamine was added 170 g (2.08 moles) 70% aqueous glycolonitrile in a fine stream while the temperature was held below 25°C by use of a cooling bath. The solution was allowed to stir at room temperature overnight and then diluted with 500 ml water. To this solution was added 138 ml (2.18 moles) 70% nitric acid while the temperature was held below 20°C. The resulting slurry was chilled to 5°C and filtered, and the product was washed sparingly with ice water. The salt was dissolved in 1500 ml water at 40 to 45°C and recrystallized on chilling. The product was again separated by filtration, washed successively with methanol and ether, and dried in a vacuum desiccator over potassium hydroxide pellets. The bis nitric acid salt of 3,6-diaza-1,8-octane dinitrile (mp., 144 to 146°C, dec) weighed 171 g, corresponding to a 62.3% yield.

(2) Preparation of 3,6-Dinitraza-1,8-octane Dinitrile

A nitrating solution was prepared by the successive addition of 5.4 ml (0.065 mole) 37% hydrochloric acid and 11 ml (0.26 mole) anhydrous nitric acid to 326 ml (3.45 moles) acetic anhydride while the temperature was held below 20°C. To this solution was added 171 g (0.648 mole) bis nitric acid salt of 3,6-diaza-1,8-octane dinitrile in portions at 30 to 35°C during a 30-min period. The mixture was stirred at 25 to 30°C for 5.5 hr, chilled to 5°C, and then diluted with 600 ml ice water. The product was collected by filtration, washed successively with ice water and methanol, and dried in a vacuum desiccator over potassium hydroxide pellets. The 105-g yield corresponded to 71.7% of the theoretical. The analytical sample of 3,6-dinitraza-1,8-octane dinitrile decomposed in the range from 176 to 195°C (depending on the rate of heating) following recrystallization from methyl ethyl ketone.

Anal. Calc'd for $C_8H_{10}O_4N_6$: %C, 31.58; %H, 3.53; %N, 36.84

Found: %C, 31.63; %H, 3.67; %N, 37.23

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(3) Preparation of 3,6-Dinitraza-1,8-octanedioic Acid

A mixture of 102.5 g (0.45 mole) 3,6-dinitraza-1,8-octane dinitrile and 510 ml 37% hydrochloric acid was gradually warmed on the steam-bath. Agitation was necessary to prevent excess frothing until the nitrile dissolved at about 75°C. Heating was continued for 3 hr at 90 to 95°C. The mixture was cooled to 20 to 25°C, and the product was collected by filtration, washed with ice water, and dried in a vacuum desiccator over potassium hydroxide pellets. The 3,6-dinitraza-1,8-octanedioic acid weighed 75 g, corresponding to a 62.7% yield. The analytical sample melted at 207 to 209°C (dec) following recrystallization from hot water.

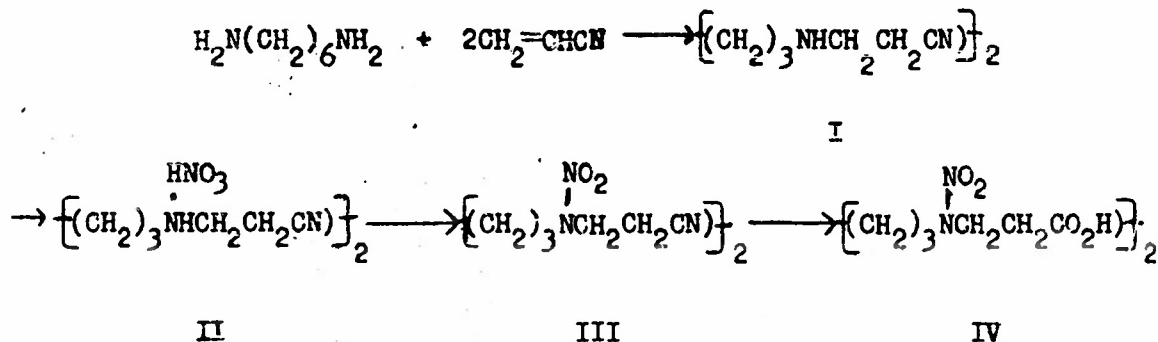
Anal. Calc'd for $C_8H_{10}O_4N_4$: %C, 27.07; %H, 3.79; %N, 21.05

Found: %C, 26.89; %H, 3.00; %N, 20.10

2. Preparation of 4,11-Dinitraza-1,14-tetradecanedioic Acid

a. Discussion

Utilizing the Michael reaction of a diamine with acrylonitrile, 4,11-diaza-1,14-tetradecane dinitrile (I), the first intermediate in the synthesis of 4,11-dinitraza-1,14-tetradecanedioic acid (IV), was obtained. This reaction and the subsequent steps in the synthesis (shown below) directly parallel the reactions involved in the preparation of the previously described 4,7-dinitraza-1,8-octanedioic acid, 4-nitraza-1,7-heptanedioic acid, and several other dicarboxylic acids containing the nitramino group.



b. Experimental

(1) Preparation of 4,11-Diaza-1,14-tetradecane Dinitrile

To 665 g (4 moles) 70% aqueous hexamethylene diamine was added 523 ml (8 moles) acrylonitrile in a fine stream with

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vigorous stirring, while the temperature was held below 40°C by means of a cooling bath. Cooling was no longer required shortly after the addition was complete, and the solution was allowed to stir at room temperature overnight. The solution was transferred to a distilling flask, and the water was removed by distillation in vacuo using an oil pump. The residue was heated to 200 to 210°C in this process. The nearly colorless residue of crude 4,11-diaza-1,14-tetradecane dinitrile weighed 810.5 g, corresponding to a 91.3% yield. The material was converted to the bis nitric acid salt without further purification.

(2) Preparation of the Bis Nitric Acid Salt of 4,11-Diaza-1,14-tetradecane Dinitrile

To a well-stirred solution of 111 g (0.5 mole) 4,11-diaza-1,14-tetradecane dinitrile in 500 ml absolute ethanol, 44.5 ml (1.04 moles) 70% nitric acid was added dropwise at 0 to 10°C. The salt was collected by filtration, washed successively with methanol and absolute ether, and dried in a vacuum desiccator over potassium hydroxide pellets. The bis nitric acid salt of 4,11-diaza-1,14-tetradecane dinitrile weighed 169.5 g, corresponding to a 97.4% yield.

(3) Preparation of 4,11-Dinitraza-1,14-tetradecane Dinitrile

A nitrating solution was prepared by the successive addition of 1 ml (0.013 mole) 37% hydrochloric acid and 3.3 ml (0.08 mole) anhydrous nitric acid to 67 (0.712 mole) acetic anhydride below 20°C. To this solution was added 69.6 g (0.2 mole) bis nitric acid salt of 4,11-diaza-1,14-tetradecane dinitrile in portions while the temperature was maintained at 20 to 30°C by intermittent use of a cooling bath. The addition of the salt was completed in a 10-min period. The salt dissolved, and with continued stirring a solid began to precipitate after approximately 15 minutes. The temperature tended to rise at all times, and intermittent cooling was required to maintain the mixture at 20°C. Since there appeared to be no further increase in the quantity of precipitated solid during an additional 15 min of stirring, the mixture was chilled to 5°C and diluted with 150 ml of ice water. The nearly colorless product was collected by filtration, washed successively with methanol and absolute ether, and air-dried. The 4,11-dinitraza-1,14-tetradecane dinitrile (mp 85 to 87°C) weighed 42.5 g, corresponding to a 68% yield. Purification by recrystallization from methanol raised the melting point to 89.5 to 90.5°C.

Anal. Calc'd for $C_{12}H_{20}O_4N_6$: %C, 46.14; %H, 6.45; %N, 26.91

Found: %C, 45.92; %H, 6.27; %N, 26.69

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(4) Preparation of 4,11-Dinitraza-1,14-tetradecanedioic Acid

A mixture of 268 g (0.86 mole) 4,11-dinitraza-1,14-tetradecane dinitrile and 2150 ml 37% hydrochloric acid was warmed on the steambath until solution occurred, and then heated at 90 to 95°C for 4.5 hours. The solution was allowed to cool to room temperature with the crystallization of the product. The latter was collected by filtration, washed with ice water, and thoroughly dried. The 4,11-dinitraza-1,14-tetradecanedioic acid weighed 242.5 g, corresponding to an 80.7% yield, and melted at 138.5 to 140°C. The melting point was not altered by repeated recrystallization from hot water.

Anal. Calc'd for $C_{12}H_{22}O_8N_4$: %C, 41.14; %H, 6.33; %N, 15.99

Found: %C, 40.97; %H, 6.13; %N, 15.74

3. Preparation of 4,7,10,13-Tetranitraza-1,16-hexadecanedioic Acid

a. Discussion

A previous report described the preparation of 7,10-dinitro-4,7,10,13-tetraza-1,16-hexadecane dinitrile and the preparation of the bis nitric acid salt of this material.* The latter compound has now been converted to 4,7,10,13-tetranitraza-1,16-hexadecane dinitrile by means of a chloride-catalyzed nitration. As could be expected for a high-molecular-weight, insoluble salt of this structure, the yield for the conversion was quite low, with the bulk of the starting material being recovered. The hydrolysis of 4,7,10,13-tetranitraza-1,16-hexadecane dinitrile in concentrated hydrochloric acid yielded 4,7,10,13-tetranitraza-1,16-hexadecanedioic acid. On the basis of previous experience in the 4,7,10-triaza-1,13-tridecane series,** it appears that the use of the bis nitric acid salt of dimethyl 7,10-dinitro-4,7,10,13-tetraza-1,16-hexadecanedioate as starting material would give a much higher percentage conversion in the nitration step.

b. Experimental

(1) Preparation of 4,7,10,13-Tetranitraza-1,16-hexadecane Dinitrile

A 30.5-g (0.065 mole) quantity of the bis nitric acid salt of 7,10-dinitro-4,7,10,13-tetraza-1,16-hexadecane dinitrile

*Aerojet Report No. 740, pp. 63-66.

**Aerojet Report No. 807.

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was added in portions at 30 to 35°C to a nitrating solution prepared by the successive addition of 1 ml (0.0012 mole) 37% hydrochloric acid and 3 ml (0.0072 mole) anhydrous nitric acid to 66 ml (0.7 mole) acetic anhydride. The resulting slurry was stirred vigorously at 30 to 35°C for 30 min and then warmed at 40 to 50°C for 1.5 hr. Following an additional period of 2 hr without warming, the mixture was chilled to 5 to 10°C, diluted with 100 ml water, and filtered. The precipitate was washed successively with water, methanol, and ether, and dried to yield 28 g solid. The latter was treated with portions of hot acetone (500 ml, total volume) to yield 20.5 g undissolved solid, which proved to be the original bis nitric acid salt of 7,10-dinitro-4,7,10,13-tetraza-1,16-hexadecane dinitrile. The 4,7,10,13-tetranitrazo-1,16-hexadecane dinitrile crystallized from the acetone solution on cooling and was collected by filtration. The product weighed 5 g and melted at 138 to 139.5°C. A second crop of crystals, weighing 1.6 g and melting at 135.5 to 138.5°C, was obtained by dilution of the acetone filtrate with diethyl ether. A sample of the larger fraction was recrystallized from acetone to yield material melting at 138.5 to 139.5°C.

Anal. Calc'd for $C_{12}H_{20}O_8N_{10}$: %C, 33.33; %H, 4.66; %N, 32.40

Found: %C, 35.00 %H, 4.70; %N, 33.70

(2) Preparation of 4,7,10,13-Tetranitrazo-1,16-hexadecanedioic Acid

4,7,10,13-Tetranitrazo-1,16-hexadecane dinitrile was hydrolyzed using 15 ml 37% hydrochloric acid per gram of dinitrile. On warming the mixture on the steam bath, the 4,7,10,13-tetranitrazo-1,16-hexadecane dinitrile dissolved at about 85°C followed by the crystallization of an intermediate, presumably the imido hydrochloride. On continued heating, further reaction again produced a clear solution during a 45-min period with the subsequent crystallization of the 4,7,10,13-tetranitrazo-1,16-hexadecanedioic acid. Heating was continued for 2 hr, the mixture was chilled to room temperature and filtered, and the product was washed with water and methanol. Recrystallization of the acid from an aqueous acetone solution gave material melting at 203.5 to 205.5°C.

Anal. Calc'd for $C_{12}H_{22}O_{12}N_8$: %C, 30.64; %H, 4.72; %N, 23.82

Found: %C, 30.55; %H, 4.85; %N, 23.55

C. NITRO-DIISOCYANATES

1. Preparation of 2,5-Dinitrazo-1,6-hexane Diisocyanate

a. Discussion

2,5-Dinitrazo-1,6-hexane diisocyanate was obtained in the usual manner by converting the acid chloride to the corresponding

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diazide followed by rearrangement of the latter material. The acid chloride, 3,6-dinitraza-1,8-octanedioyl chloride, was prepared from the corresponding acid by the use of thionyl chloride and by the use of phosphorous pentachloride. Thionyl chloride was not a satisfactory reagent for this particular conversion, as the unreactivity or insolubility of the acid coupled with the relative instability of the acid chloride made the yield very low. 2,5-Dinitraza-1,6-hexane diisocyanate appears to be a very desirable diisocyanate for use in polyurethane formation from the standpoint of high energy availability. The polyurethane obtained from 2,5-dinitraza-1,6-hexane diisocyanate and 2,2-dinitro-1,3-propanediol has a calculated specific impulse of 197.5 lbf sec/lbm, and the corresponding post-nitrated polymer has a calculated specific impulse of 236.6 lbf sec/lbm.

b. Experimental

(1) Preparation of 3,6-Dinitraza-1,8-octanedioyl Chloride

(a) A mixture of 74.5 g (0.28 mole) 3,6-dinitraza-1,8-octanedioic acid and 300 ml thionyl chloride was heated on the steam-bath at reflux temperature for 4 hr. The acid did not completely dissolve during this time, but as the solution had darkened considerably, further heating did not appear to be advantageous. The undissolved acid (25 g) was removed by filtration. Since the product did not separate from the filtrate on chilling, the thionyl chloride was removed by distillation in vacuo. The crude residue was dissolved in methylene chloride, and the product crystallized on chilling. The acid chloride was removed by filtration and washed with absolute ether. The ether washings caused the precipitation of a considerable quantity of highly colored reddish oil from the methylene chloride. The acid chloride weighed 22 g after removal of solvent and melted at 87.5 to 91.5°C.

(b) A mixture of 25 g (0.094 mole) 3,6-dinitraza-1,8-octanedioic acid, 62 g (0.3 mole) phosphorous pentachloride, and 50 ml phosphorous oxychloride was warmed on the steam-bath. The acid dissolved fairly rapidly, with evolution of hydrogen chloride. At the end of a 15-min period at 90°C some gas continued to be evolved; but since the solution appeared to darken quite rapidly at this temperature, heating was discontinued. The phosphorous oxychloride was removed by distillation in vacuo, and the 36-g residue was recrystallized from methylene chloride. The product weighed 13 g after drying. A sample of the product was recrystallized three times from dry, alcohol-free chloroform to give a colorless material melting at 105 to 106.5°C.

Anal. Calc'd for $C_8H_8O_6N_4Cl_2$: %C, 23.78; %H, 2.66; %N, 18.49; %Cl, 23.40

Found: %C, 24.31; %H, 2.85; %N, 17.94; %Cl, 23.23

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A sample of the acid chloride was converted to dimethyl 3,6-dinitraza-1,8-octanedioate by warming briefly with methanol. The dimethyl ester melted at 24 to 25°C.

Anal. Calc'd for $C_8H_{14}O_8N_4$: %C, 32.66; %H, 4.80; %N, 19.04; %OCH₃, 21.10

Found: %C, 32.51; %H, 4.67; %N, 18.66; %OCH₃, 20.83

(2) Preparation of 2,5-Dinitraza-1,6-hexane

Diisocyanate

A solution of 19.7 g (0.065 mole) 3,6-dinitraza-1,8-octanedioyl chloride in 300 ml ethylene dichloride was added in a fine stream with vigorous stirring to a solution of 13 g (0.2 mole) sodium azide in 35 ml water while the temperature was held at 5 to 10°C. The 3,6-dinitraza-1,8-octanedioyl azide did not dissolve in the ethylene dichloride as had been expected, but crystallized from solution. The mixture was allowed to stir for 1.5 hr at 5°C, and the dense crystals of the azide were removed by filtration and washed successively with ice water, methanol, and absolute ether. The azide was dampened with ethylene dichloride, transferred to a distilling flask, and suspended in 300 ml ethylene dichloride. A portion of the solvent was removed by distillation in vacuo to insure complete removal of moisture, and the azide was then rearranged on warming the mixture on the steam-bath at atmospheric pressure. The azide dissolved at 45 to 50°C, and decomposition began at 60 to 65°C. Heating was continued for 45 min, and the solvent was distilled in vacuo until crystals of the diisocyanate began to separate from solution. The mixture was then chilled, and the diisocyanate was collected by filtration, washed with absolute ether, and dried. The diisocyanate weighed 9.5 g and melted at 95 to 98°C. Two recrystallizations from ethylene dichloride raised the melting point to 98 to 100°C.

Anal. Calc'd for $C_6H_8O_6N_4$: %C, 27.70; %H, 3.10; %N, 32.31

Found: %C, 27.70; %H, 3.21; %N, 31.90

The dimethyl urethane, dimethyl 4,7-dinitro-2,4,7,9-tetraza-1,10-decanedioate, was prepared by treatment of the diisocyanate with methanol. This urethane melted at 169 to 171°C.

Anal. Calc'd for $C_8H_{16}O_8N_6$: %C, 29.63; %H, 4.97

Found: %C, 29.61; %H, 4.83

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2. Preparation of 3,10-Dinitraza-1,12-dodecane Diisocyanate

a. Discussion

3,10-Dinitraza-1,12-dodecane diisocyanate was prepared for the purpose of comparing the physical properties of the polyurethanes and post-nitrated polyurethanes from this long-chain diisocyanate with polymers previously prepared from the diisocyanates of similar structure but shorter chain-length. The diisocyanate was obtained by rearrangement of 4,11-dinitraza-1,14-tetradecanedioyl azide in ethylene dichloride. The azide was obtained by the action of sodium azide on the corresponding acid chloride. The latter was prepared from 4,11-dinitraza-1,14-tetradecanedioic acid by the use of thionyl chloride.

b. Experimental

(1) Preparation of 4,11-Dinitraza-1,14-tetradecanedioyl Chloride

A mixture of 32 g (0.0914 mole) 4,11-dinitraza-1,14-tetradecanedioic acid and 128 ml thionyl chloride was warmed on the steam-bath. The acid reacted quite readily, with complete solution in a short period. Heating was continued for a total heating period of 1 hr. The thionyl chloride was distilled *in vacuo*, and the residue was triturated with absolute ether, filtered, and dried. The 4,11-dinitraza-1,14-tetradecanedioyl chloride (mp 67 to 70°C) weighed 31.5 g, corresponding to an 89% yield. Recrystallization from ethylene dichloride and ether mixtures yielded a purified sample melting at 66.5 to 68.5°C.

Anal. Calc'd for $C_{12}H_{20}O_6N_4Cl_2$: %C, 37.22; %H, 5.21; %N, 14.47; %Cl, 18.31

Found: %C, 37.33; %H, 5.30; %N, 14.41; %Cl, 17.63

The acid chloride was converted to dimethyl 4,11-dinitraza-1,14-tetradecanedioate by treatment with methanol in a fairly concentrated solution. Two recrystallizations from absolute ether yielded product melting at 47 to 47.5°C.

Anal. Calc'd for $C_{14}H_{26}O_8N_4$: %C, 44.44; %H, 6.93; %N, 14.81; %OCH₃, 16.40

Found: %C, 43.76; %H, 6.59; %N, 14.60; %OCH₃, 16.15

(2) Preparation of 3,10-Dinitraza-1,12-dodecane Diisocyanate

A solution of 27 g (0.07 mole) 4,11-dinitraza-1,14-tetradecanedioyl chloride in 150 ml dry ethylene dichloride was added in a fine stream to a vigorously stirred solution of 13.7 g (0.21 mole) sodium azide in 35 ml water at 5°C during a 15-min period. The mixture

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was immersed in an ice bath, and stirring was continued for 75 minutes. It had been expected that the diazide would be soluble in ethylene dichloride, but the product crystallized from solution. The material was removed by filtration, washed successively with ice water, methanol, and absolute ether, and transferred to a flask for rearrangement. On the addition of 250 ml dry ethylene dichloride to the 21 g diazide (very slightly damp with ether), the material dissolved, indicating that the diazide is somewhat soluble in this solvent and that a portion of the product had been discarded with the original ethylene dichloride solution. The solution was distilled briefly in vacuo (100 ml distillate), and the azide was then rearranged on warming the solution on the steam-bath at atmospheric pressure. With the evolution of nitrogen complete, the solvent was distilled in vacuo. The solid residue was triturated with absolute ether, filtered, and dried to yield 15.7 g crude 3,10-dinitraza-1,12-dodecane diisocyanate. Recrystallization from an ethylene dichloride-ether solution gave a nearly colorless product melting at 75 to 76°C.

Anal. Calc'd for $C_{12}H_{20}O_6N_6$: %C, 41.85; %H, 5.85; %N, 24.41

Found: %C, 41.54; %H, 5.59; %N, 24.86

The dimethyl urethane was formed by treatment of the diisocyanate with methanol. This highly insoluble product was recrystallized from a very dilute methanol solution to give colorless crystals melting at 164.5 to 166°C.

Anal. Calc'd for $C_{11}H_{28}O_8N_6$: %C, 41.17; %H, 6.91; %N, 20.58; %OCH₃, 15.20

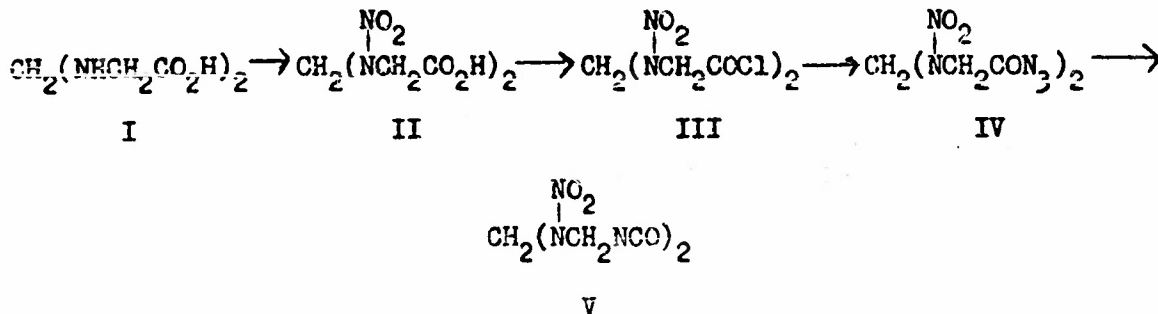
Found: %C, 40.84; %H, 6.64; %N, 21.02; %OCH₃, 14.99

D. INTERMEDIATES

1. Attempted Preparation of Methylendiglycine

a. Discussion

The following series of reactions indicates the proposed method of obtaining the very desirable diisocyanate, 2,4-dinitraza-1,5-pentane diisocyanate, from methylenediglycine (3,5-diaza-1,7-heptanedioic acid).



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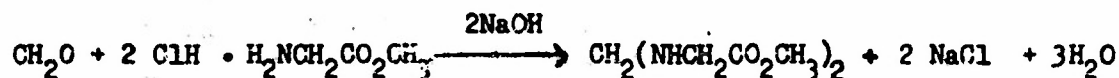
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Unfortunately, the literature contains but a single reference to the preparation of methylenediglycine, and it has not been possible to repeat this synthesis successfully.* The reported preparation involved the Mannich condensation of formaldehyde with two moles of glycine in hydrochloric acid solution to yield the bis hydrochloride of methylenediglycine. On repeating this synthesis, an apparent mixture was obtained which failed to yield a water-insoluble product on nitration. When the condensation was attempted in the presence of nitric acid, the sole product was the nitric acid salt of glycine. An attempt was also made to effect the condensation of methyl glycine (methyl aminoacetate) and formaldehyde.



A viscous, water-soluble oil was obtained from this condensation, and nitration yielded a viscous, water-insoluble oil. Neither of these products has been identified.

*N. Löb, Biochem. Z. 51, 122 (1913).

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APPENDIX A

MANUFACTURE OF NITROPOLYMERS

Figure 1 shows a nitropolymer sheet after removal of the solvent, Figure 2 shows mixing of plasticized nitropolymer with inorganic-oxidizer on the roller mill, and Figure 3 shows the extrusion of plasticized nitropolymer-inorganic oxidizer formulation.



Figure 1

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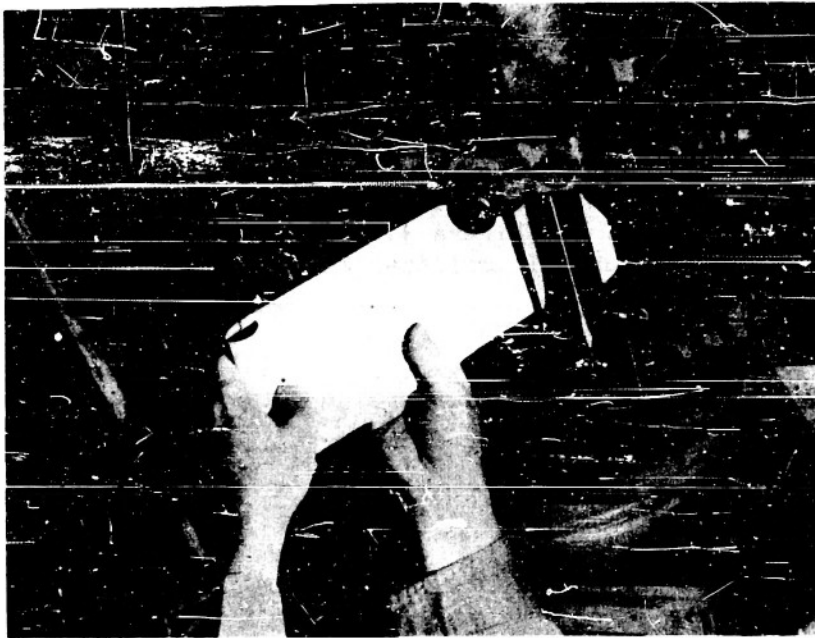


Figure 2

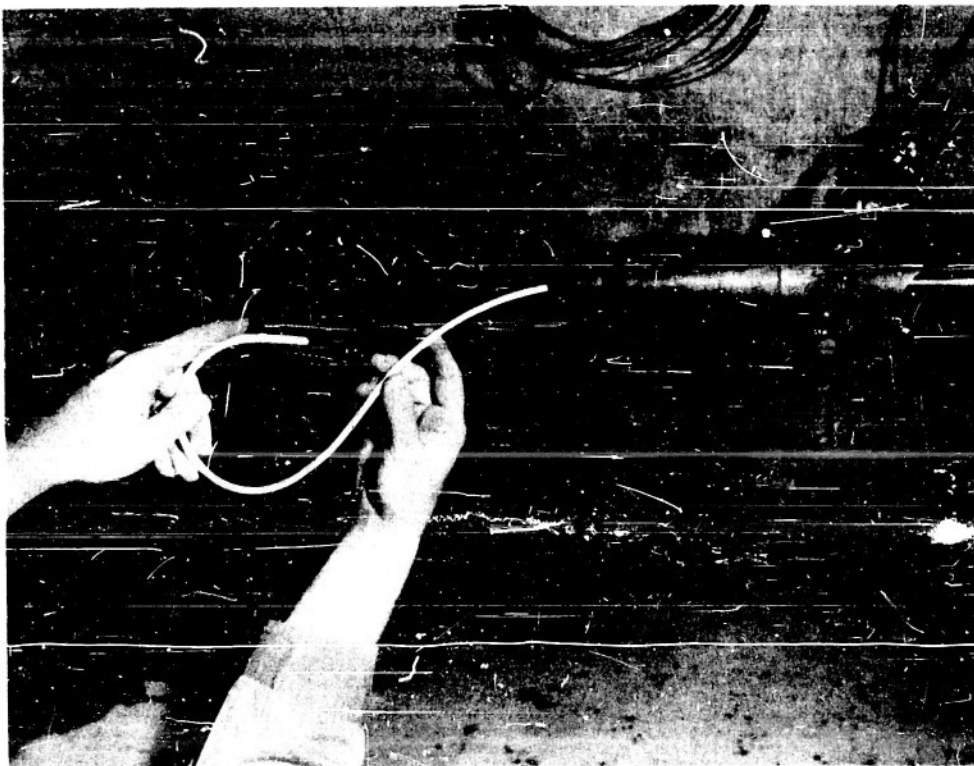


Figure 3

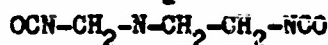
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Data Questionnaire on

COMPOUNDS FOR USE AS INGREDIENTS OF PROPELLANTS AND OTHER EXPLOSIVES

Listed below are the characteristics which are believed to be of importance in the study of a compound which may possibly be used as a constituent of solid propellants or other explosives. It is not expected that all this information will be available for every compound. For example, with a compound showing poor stability, it is probably not advisable to investigate that compound farther. After placing such information as is available for a compound which you have prepared or tested on one of these forms, send it to SOLID PROPELLANT INFORMATION AGENCY, AFL/JHU, 8621 Georgia Avenue, Silver Spring, Maryland. As additional information on the same or new compounds accrues, forward it on a similar form at a later date. The information submitted on these forms will be rewritten and published by SPIA in loose-leaf manual form. These forms may also be used as work or data sheets for your experimental studies. Extra copies are available upon request from SPIA. Suggestions for improvement of these forms are invited. If insufficient space has been provided for any item, attach separate sheets.

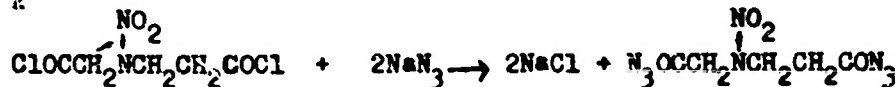
COMPOUND:

Name 2-Nitrazo-1,4-butane diisocyanateEmpirical formula C₄H₆N₂O₂Structure: (configuration) 3 6 4 4NO₂

Information submitted by:

Activity Aerojet General CorporationPerson C. Vanneman, R. ParretteDate 7 May 1954

Preparation reaction(s):



1. Quantitative analysis (% by weight)	<u>N₃OCCH₂NCH₂CH₂CON₃</u>	<u>→</u>	<u>OCNCH₂NCH₂CH₂NCO</u>	<u>+ 2N₂</u>
	Carbon	Hydrogen	Oxygen	Nitrogen
Calculated from formula	<u>32.26</u>	<u>3.25</u>	<u>30.10</u>	<u>30.08</u>
By determination	<u>32.20</u>	<u>3.06</u>	<u>30.08</u>	<u>30.08</u>

Assay with di-n-butyl amine; 98.55%, 98.13% (duplicate analyses)

2. Burning properties: (compared to nitrocellulose, under nitrogen at atmospheric pressure:)

(faster? slower? residus? etc.)

3. Stability and Sensitivity: Plot any graphs on separate sheet

Discuss methods used when they vary from references. Give temperature used. (Use separate sheet if necessary.)

Name of test	Recommended method
a. Impact Sensitivity	OSRD 3185
b. Thermal Stability	OSRD 3401 p.8 <u>134.5°C, methyl violet paper.</u>
c. Vacuum Stability	OSRD 3401 p.10
d. Temperature of Explosion	OSRD 3401 p.6
e. Temperature of Ignition	OSRD 3401 p.6
f. Thermal Stability, <u>65.5°C</u>	<u>Picatinny Arsenal No. 1401. 1.3-g sample, KI-starch paper.</u>
g. Impact Stability	<u>Bureau of Mines Bull. No. 346, 2-kg. wt., 50% shots.</u>
h.	

RESULTS OF ABOVE TESTS

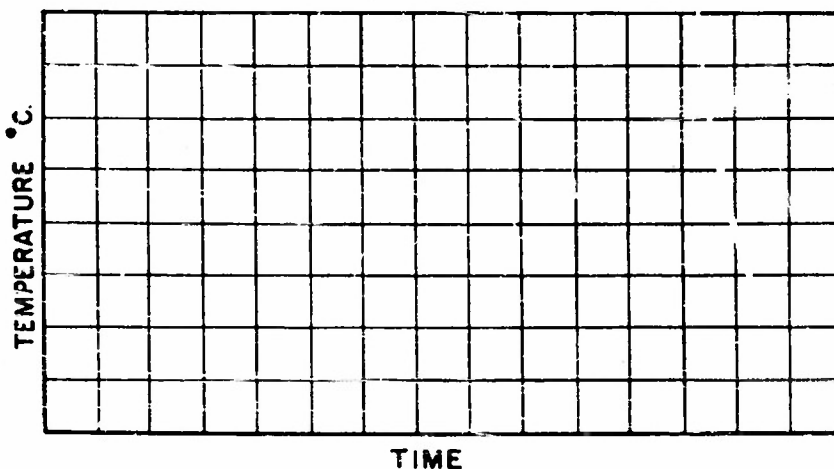
Reference compound (designation-TMT, Tetryl, N.C., etc.)	New Compound test results
a.	
b. Nitrocellulose, 30 min. no color.	<u>Colored. Fumed off, 16 min</u>
c.	
d.	
e.	
f. Nitrocellulose, 10 min. no color	<u>Colored. Fumed off, 3 1/2 hr</u>
g. RDX, 28 cm; composition A, >100 cm.	<u>> 100 cm</u>
h.	

4. Heat of formation: (ΔH) + -25 Kg. calories at 25°C., 1 atm. pressure
(Indicate sign)

	By Experiment	By Calculation	Method
5. Energy of explosion (Q) (at 25°C. H ₂ O liquid)		cal/gm	Description or reference. Separate sheet if necessary.
6. Heat of combustion (H _c) (at 25°C. H ₂ O liquid)	3367	cal/gm	3494 Aerojet Report 417A.
7. Specific impulse (I _{sp}) calc:		lb-sec/lb	
8. Physical form of compound (viscous liquid, crystalline type, etc.)	Viscous, clear liquid, or white solid below melting point.		
9. Simple microscope analysis data: (crystal studies)			
10. Density (Macro method)	1.402 gm/cm ³ .	(Micro or other method)	gm/cm ³ .
(Explain on separate sheet any unique methods you use.)			
11. Index of refraction: (n _D ^{25°C.})	1.5037	12. Color	Colorless
		13. Odor	None
14. pH at 25°C.	(Method reference OSRD 3401 p.4, or OSRD 5968. Indicate method used, i.e., solvent and concentrations used. pH indicator paper or Beckman pH meter.)		
15. Hygroscopicity:	New Compound	Reference Compound	(designation)
Visible change on exposure to ambient air.	Hydrolyses, forms polyurea.		
% wt increase by* (a) or (b)			
(Strike out method (a) or (b) if not used.)	(If other than below methods are used, explain on separate sheet.)		
*Method:			
<p>(a) The sample (approx. 5-10 g. of whole grain small powder or 1 grain of large powder) is placed in a glass weighing bottle. The weighing bottle (cover removed) is placed in a vacuum drying oven for 5 hrs. @ 55°C. Remove weighing bottle from oven, cover with glass stopper, cool in a desiccator and weigh accurately. This is taken as original dry weight of sample. Then place weighing bottle (cover removed) in a humidifier (a 10-in. desiccator is a satisfactory vessel) containing 1 liter of 18.6 ± .5% H₂SO₄. (This gives relative humidity 90 ± .25%). Place in an oven maintained at 30 ± 2°C. On the fourth day remove weighing bottle from the humidifier, cover with glass stopper, cool in a desiccator and weigh. Then return to humidifier for 24 hours, cool and reweigh. Continue daily weighings until constant weight indicates sample has reached equilibrium with 90% R.H. The % weight increase is then reported as hygroscopicity of the sample.</p> <p>(b) An alternate method is in OSRD 3401 p.3.</p>			
16. Volatility: Report as rate of loss in wt % per unit area (for liquid samples measure the surface area; for solids, the sample should be screened between 100-120 mesh U.S. Standard certified sieve) per 4 hrs., after constant rate of loss is obtained during three consecutive 4-hr. periods at (a) 25°C in a vessel through which a stream of dry air is forced, (b) in an oven at 65.5°C or (c) under other test method or conditions.			
(Description or reference to other test or conditions used. Use separate sheet if necessary.)			
Volatility results on:	New Compound	Reference Compound	(designation)
a.		a.	
b.		b.	
c.		c.	
17. Boiling point, or decomposition temperature: (underline which temperature is reported)			
18. Heat of Vaporization:		g-cal./gm	BTU/lb.
19. Heat of Fusion:		g-cal./gm	BTU/lb.
20. Melting point:	1 to 2 °C.		

21. Freezing point vs. Time Curve: (Please mark the coordinates with scale values that apply to the compound under study.)

Hydrolyzes, polymerizes at melting point

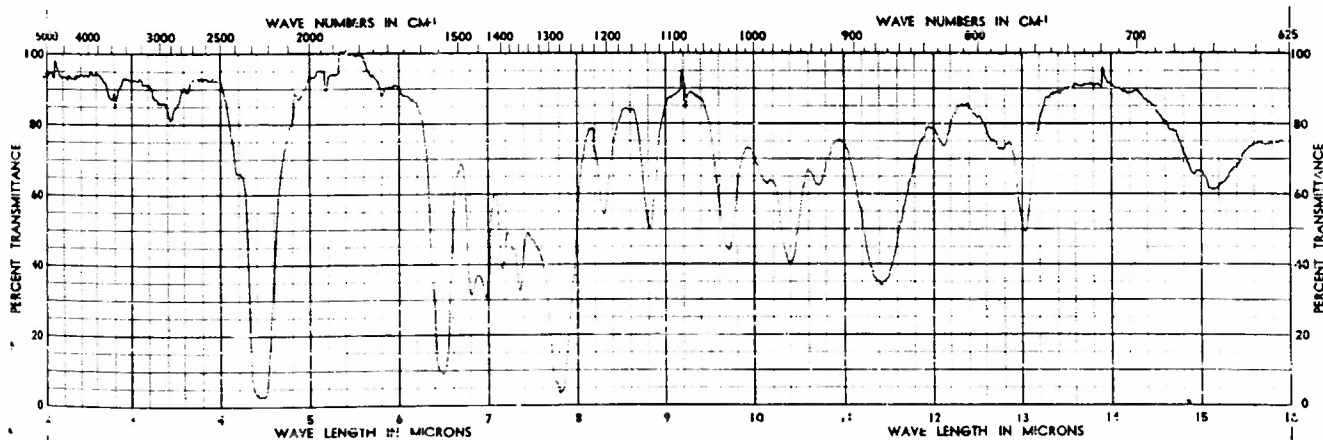


22. Solubility of new compound:

_____ g/100 ml H₂O at 25°C. _____ g/100 ml H₂O at _____ °C.
_____ g/100 ml n-heptane at 25 °C.
_____ g/100 ml (name material used as solvent)
_____ g/100 ml carbon tetrachloride at 25 °C.
10.8 g/100 ml ether at 25 °C.

Miscible with chloroform, methylene chloride, dioxane, ethyl acetate, benzene, and toluene. Reacts with water and alcohols. Can be recrystallized from absolute ether.

23. Infrared spectrum:



2-Nitrazo-1,4-butane diisocyanate - Assay No. 454, NaCl cell, no spacer.- 12-min scan. 2/23/54.

Under compatibility we are considering the ability of two compounds to be in intimate contact (Note OSRD 5758 p. 21-22) over a long period of time without adverse effects on either the chemical or physical properties of either material. These tests will probably be of varied extent. They might be some of the following: (a) Standard stability tests. (b) Simple observations of exudation or separation at ambient or accelerated temperature. (c) Prepare thin sheets (.025" thick, 1" square) of the plasticized material. Separate the sheets with strips of cigarette paper or carbon paper and compress the stack in a "C" clamp. After several days note the oily collection on the paper. Please give reference to or describe procedure used. Item 26 is to indicate results when the compound is in contact with some material other than ethyl cellulose, nitrocellulose or rubber. Test performed by dissolving sample and standard in a common solvent, drying rapidly on a glass plate, and examining the resulting film for clarity and homogeneity.

25. Compatibility with ethyl cellulose: _____

26. Compatibility with nitrocellulose: Ratio, wt sample/wt NC

<u>20/80</u>	<u>compatible</u>
<u>50/50</u>	<u>compatible</u>
<u>80/20</u>	<u>compatible</u>

27. Compatibility with rubber: Ratio, wt sample/wt rubber

<u>20/80</u>	<u>compatible</u>
<u>50/50</u>	<u>compatible</u>
<u>80/20</u>	<u>incompatible</u>

28. Compatibility with _____:

29. Polymerizing properties of the new compound:

(a) By itself Can be preserved if kept dry under refrigeration.

(b) In mixtures (with additives) Copolymerizes with dialy. to form polyurethanes.

(c) Inhibiting action on polymerization of:

Thiokol _____

Methacrylate _____

Other compounds _____

30. Availability

a. Amount now available? Research quantities.

b. When was available material first prepared? _____

c. Amount prepared at that time? _____

d. Is large production feasible? _____

e. Plant capacity in existence, lbs/day? _____

f. Outline steps for a quantity production method _____

31. Additional information: (toxicity, hazards, deterioration, oxygen balance, detonation rate, explosive power, ease of hydrolysis by water, etc. List references, reports, data books, etc. that refer to the compound.) _____

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